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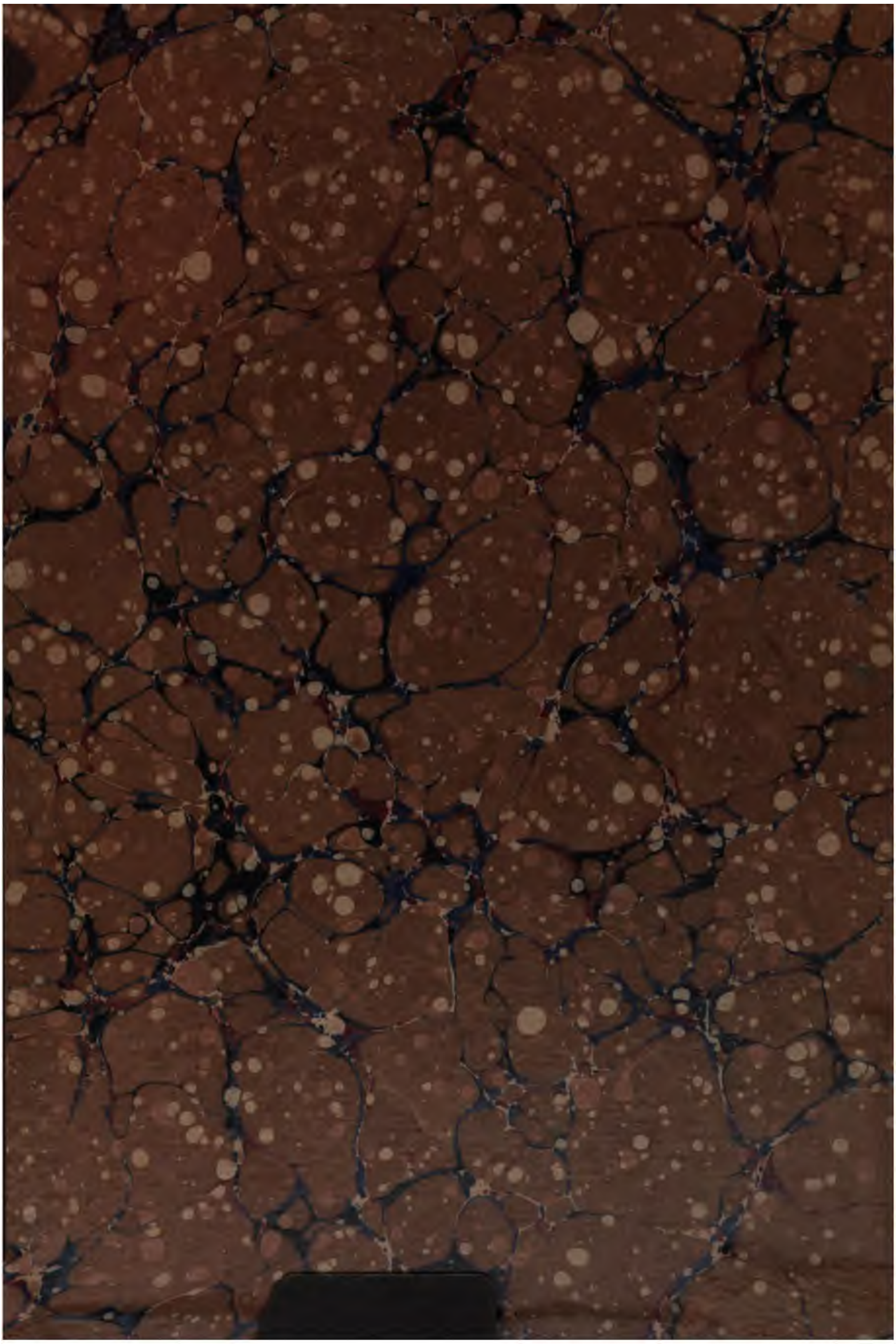

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The Electromotive Force of Iron Under Varying Conditions, and the Effect of Occluded Hydrogen

BY

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THE ELECTROMOTIVE FORCE OF IRON UNDER VARYING CONDITIONS, AND THE EFFECT OF OCCLUDED HYDROGEN.

The topics named in the title of this paper are of great practical importance, as well as of great interest from the theoretical point of view. The rate of rusting and the change of properties caused by the occlusion of hydrogen are essential factors in determining the permanence and strength of most modern buildings, bridges, and underground pipes. For this reason the literature which has already accumulated upon the subject has grown almost to the dimensions of a library in itself. The theoretical side of the matter also is of great interest. The cause of the sudden diminution of activity produced in iron under certain well-known circumstances has not yet found its definitive explanation, and the mechanism of the occlusion of hydrogen by a solid so tenacious and compact as iron is a theoretical question of no small interest.

Phenomena relating to these topics are considered together in this paper, because the method of investigation furnished evidence with regard to both. The matter was considered rather from the theoretical than the practical standpoint. The method was the determination of the electromotive force of iron, after subjection to a great variety of changing conditions, on immersion in a solution of one of its salts, in order by comparison of these different values of electromotive force to draw inference concerning the state of the metal and its occluded gas.

The object of the research, as originally planned, was to add to the experimental evidence concerning the significance of changing atomic volume, and it was proposed to discover whether or not changes in free energy were associated with changes of density and of other properties of the solid. During the progress of the work it was found that this matter could not be satisfactorily studied without studying the properties of occluded hydrogen, because, in spite of the great volume of literature upon the subject, certain important questions seemed to have remained hitherto almost untouched. Lack of time has as yet prevented the completion of the program; but the present results, although only a part of the whole plan, are reasonably complete in themselves, and therefore worthy of separate publication. The subject will be taken up again in the near future.

For the sake of clearness and convenience, the present paper will be divided into two parts, entitled: Part I. "The Electromotive Force of Pure Iron under Varying Conditions;" Part II. "The Electromotive Force of Iron Containing Occluded Hydrogen."

PART I. THE ELECTROMOTIVE FORCE OF PURE IRON UNDER VARYING CONDITIONS.

When in a definite state of internal equilibrium, the electromotive force of a metal immersed as a reversible electrode in a definite solution of one of its salts must have a perfectly definite value under given conditions. A change in the internal state must of necessity change this electromotive force, unless the temperature happens to be exactly at the transition point. For this reason it seemed not improbable that the measurement of the electromotive force of iron which had been subjected to great stress would afford the most convenient method of determining whether or not this stress had affected a permanent alteration in the internal equilibrium of the metal, a " permanent set," as it is sometimes called, or an extraordinary condition of metastable equilibrium.

A solid may be subjected to a variety of stresses. The first which it seemed desirable to study was direct pressure, in order to determine if this pressure, by causing closer internal structure, diminishes the outward or dissolving tendency as measured by electromotive force, or if, on the other hand, the substance, when released from the pressure, returns at once to essentially the state in which it was before the pressure was applied. Experiment alone could decide between these alternatives.

It was desirable also to test the possibly opposite effect of a negative pressure, a distending tendency, such as the effect of stretching a wire to the breaking-point. This effect was also made the subject of experiments recorded below.

During these tests it was found that the temperature used in the reduction of the iron from its oxide caused a very important effect on the dissolving tendency, and therefore this matter also had to be considered in a special series of experiments.

PREPARATION OF MATERIAL.

In any research with iron it is of primary importance that the substance experimented upon should be pure—free from carbon, silicon, sulphur, phosphorus, manganese, and, as the following work testifies, from hydrogen also.

Most of the iron used in this research was prepared by a method which had been found in an exhaustive investigation of the atomic weight of the metal to yield good results.[1] It is true that not quite all the steps were used in the present work, but the more essential ones were retained, and a very pure sample of the metal was prepared. "Piano" wire of good quality served as the original substance; it was carefully sandpapered and wiped, and dissolved in dilute nitric acid. Concentrated acid was first used, but this oxidized the silicon to silicic acid, and filtration from the silicon itself (or silicide of iron, $SiFe_2$),[2] which the dilute acid leaves unchanged, was considered more safe, besides being more convenient. All iron carbide or graphite is either completely oxidized or else is unchanged and filtered out. The dilute acid also lessens the chances of any sulphur being oxidized to sulphate.

The nitrate formed was then concentrated and recrystallized three or four times. Recrystallization is here a peculiarly good method of purification, because the ferric nitrate has an unusual crystal form; therefore most impurities can only be held mechanically.[3] The recrystallized salt was then heated in a platinum dish at a moderate temperature in an electric oven. The nitric acid was partly driven off and the dry, dark-red basic nitrate was then powdered in a Hempel steel mortar[4] and heated to full redness to complete the denitration. It is important that this operation be carried out in steps as described, because in this way a fine, spongy powder is obtained which allows of perfect reduction. If denitrated too quickly by too high a temperature the oxide obtained is exceedingly hard and the powder consists of very compact particles, in which the complete reduction of the core is more or less uncertain and decidedly less rapid.

The oxide so produced was reduced in a stream of electrolytic hydrogen[5] in an unglazed porcelain boat[6] set in a hard glass combustion-tube when a low-temperature reduction was desired, or in a large glazed porcelain tube[7] in a gas-furnace when a higher temperature was used.

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[1] Richards and Baxter, Z. f. anorg. ch., **23**, 245 (1900); Proc. Amer. Acad., **35**, 253 (1900).

[2] Lebeau, Bull. Soc. Chim., Paris, (3) **27**, 39-42 (1902); Ann. Chim. Phys. (7), **26**, 5-31 (1902).

[3] T. W. Richards, Zeitschr. f. phys. Chem., **46**, 189 (1903).

[4] W. Hempel, Z. f. ang. Chem. **14**, 843 (1901).

[5] The generators used were zinc amalgam, dilute hydrochloric acid, platinum cells, and were of the convenient form used by Cooke and Richards, Proc. Amer. Acad. **23**, 168 (1887). The hydrogen was twice washed in strong caustic solution and dried by passing through two caustic potash towers.

[6] Unglazed, because at the high temperature used the glaze frequently fused with the iron.

[7] Hempel water-cooled stoppers were used in the porcelain tube.

The iron from these reductions was of a gray color and of a porous structure. A piece of it could usually be broken with ease between the fingers and rubbed to powder. This consistency was of course due to its mode of preparation, the powdered oxide having been simply pressed into the boats and the temperature having been only high enough to cause slight cohesion between the particles, not to fuse the mass.

The cohesion of the particles varied considerably with the temperature at which the reduction was carried on, a product reduced at 600° having no cohesion at all, while one heated to about 1,100° for some time could be broken only with some difficulty. The color also varied, owing to the difference in degree of subdivision, from almost black to a clear, silvery gray.

A convenient index of complete reduction was the absence of any trace of black oxide in the cooler portions of the boat; for water formed in the hotter places is decomposed in the somewhat cooler ones, and if the reduction is not complete water is of course present. Ordinarily, the reduction was carried out by heating the substance in a rapid stream of hydrogen for three or four hours with a Bunsen burner, and then for about half an hour at the highest temperature of the blast lamp. Such iron showed not the slightest trace of black oxide, even when finely powdered in a mortar. After heating the iron remained in a continuous stream of dry hydrogen until quite cold, and was then transferred for preservation to a good desiccator containing finely divided fused caustic potash. No trace of oxidation was ever visible on iron thus preserved; but, as will be explained later, the electromotive force measurements gave clear evidence that an exceedingly thin coating of oxide or adsorbed oxygen had been formed, and therefore, for the more accurate experiments, small boat-loads of pieces about the size of peas were reduced a second time and sealed in hydrogen until just before using, thus avoiding the possibility of oxidation. Whenever this specially sealed iron is used in the experiments below the fact is mentioned. The sealing was done as follows: A hard glass tube was drawn out in several places, having between each contracted place a boat containing porous iron. Three or four such boats in series were laid in a combustion furnace, and after reduction the boats were sealed off by drawing out the contracted places.

All this iron undoubtedly contained hydrogen in greater or less amounts. Although, as Baxter[1] has shown, the *weight* of hydrogen retained by pure iron ignited at a high temperature is inconsiderable, some of the other properties of the occluded gas are more important, as will be seen. Most of the hydrogen can be expelled by heating for a long time in vacuum, or by standing for a long time in dry air; but in order to drive out the last traces fusion in vacuum is necessary.

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[1] Baxter, Am. Chem. Journ., **22**, 363 (1899).

METHOD OF MEASUREMENT.

The solution-tension of the iron was measured as its electromotive force in a normal solution of ferrous salt, in this case ferrous sulphate. The sulphate ion is desirable here, since it is neutral as regards passivity phenomena, having neither passivizing nor activizing effect.[9] The voltage of the cell Fe, $n\mathrm{FeSO_4}$, $n/10\mathrm{KCl}$, HgCl, Hg, was measured by the well-known compensation method of Poggendorff.[10]

A d'Arsonval galvanometer served as zero instrument, being sensitive to 0.001 volt with the resistance used. A Helmholtz cell was used as a standard of comparison. Its exact value was 0.993 international volt, as determined by a comparison with carefully prepared cadmium normal elements. These agreed accurately among themselves, and were assumed to possess at 21.50° C. the value 1.0185 volts. They agreed also with the standards of the Jefferson Physical Laboratory.

As a standard electrode the mercury-calomel-potassium chloride electrode first suggested by Ostwald[11] was considered the best for the reasons he so convincingly puts forward in his argument with Wilsmore.[12] In the present research tenth normal instead of normal potassium chloride was usually used as the electrolyte. All values of electromotive force are given for the whole cell, Fe, $\mathrm{FeSO_4}$, KCl, HgCl, Hg, a definite measurable quantity, instead of for the single potential difference Fe, $\mathrm{FeSO_4}$, because of the uncertainty as to the absolute value of the decinormal electrode. If 0.56 volt is supposed to be the value of the normal calomel electrode, the value 0.612 volt for the tenth-normal electrode should be used, as recently determined by Sauer[13] and verified by us. Subtracting this from the values given, a value comparable to the commonly accepted values of single potential differences will be obtained.

A special arrangement of the decinormal electrode was adopted, in order to prevent its contamination with iron. To the connecting-tube, used for immersion in the ferrous sulphate cell, was attached above a siphon-inlet from a large bottle of decinormal potassium chloride on the shelf above. The fact that it was possible to wash out the tube of the decinormal electrode by means of this fresh solution removed the possibility of variation through the backward diffusion of normal ferrous sulphate or other electrolyte. By means of this arrangement one such electrode lasted through a whole season and at the end of that time gave no test for iron in the cell itself. Thus the uncertainty of this possible error is removed and the nuisance of repeated renewal of the electrode done away with. The arrangement is shown on the left-hand side of figure 1.

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[9] Sackur, Z. f. Electrochem., **10**, 843 (1904).

[10] Ostwald-Luther, Physico-Chemische Messungen, p. 367.

[11] Lehrbuch, **2**, 945 (1893).

[12] Z. f. Physik., ch. **35**, 333 (1900); ibid., **36**, 91 (1901).

[13] Z. f. Physik., ch. **47**, 184 (1904). That is, $N/10$ electrode = 0.612 volt if the $N/1$ electrode is called 0.560 volt.

The usual arrangement of the iron and of the cell was as shown in figure 1, and on a larger scale in figure 2. The sample, about half the size of a pea, was inserted in a running noose of platinum wire, the end of which projected through a fine hole in a cork stopper. The noose was then pulled tight, drawing the sample against the cork, and the wire was fastened by winding around the shank of an iron tack on the other side of the cork. The cork was fitted into one end of a glass tube and carefully sealed with molten paraffin. The tube was filled with normal ferrous sulphate solution by

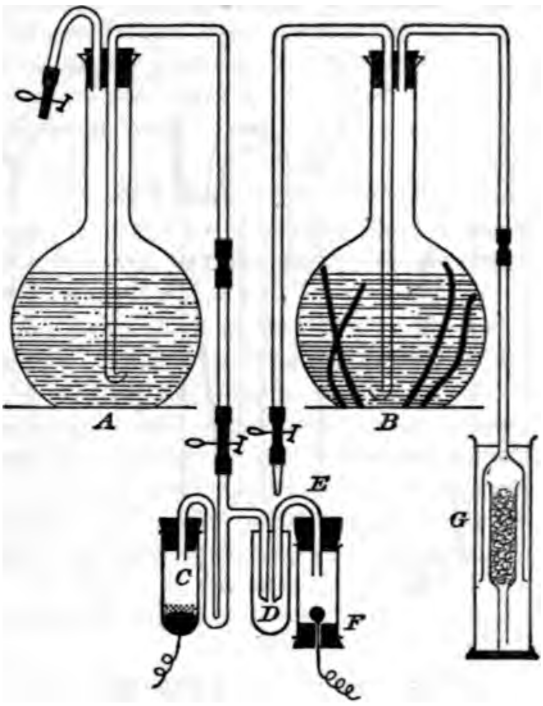

FIG. 1.—THE CELL AND ITS APPURTENANCES.

A. Reservoir of decinormal potassic chloride.
B. Reservoir of normal ferrous sulphate containing pure iron wires.
C. Calomel electrode (decinormal).
D. Connecting receptacle containing ferrous sulphate.
E. Inverted U tube.
F. Iron electrode (enlarged in fig. 2).
G. Automatic hydrogen generator, protecting Reservoir B from air.

means of a siphon from the reservoir, and an inverted U-tube and stopper were inserted in the top to make connection with an open test-tube containing ferrous sulphate fastened alongside by means of a rubber band. In this way the iron was kept for some time safe from oxidation, yet always open to measurement. The arrangement is illustrated in figure 2. When the end of the tube of the decinormal electrode (*C* in figure 2) was dipped into this test-tube full of ferrous sulphate, the cell was complete and ready for measurement. A large number of "iron electrodes" could be placed around the sides of the thermostat, all attached to one wire, and the change of connection from one cell to another was made by simply lifting the iron stand to which the decinormal electrode was attached and dipping the end of the standard electrode's tube into the next test-tube. Thus a large number of measurements could be taken with a minimum expenditure of time and trouble, a very necessary matter in an investigation involving thousands of measurements. The thermostat, electrically regulated and heated, in which the electrode was immersed, was kept at 20.0° C. The normal ferrous

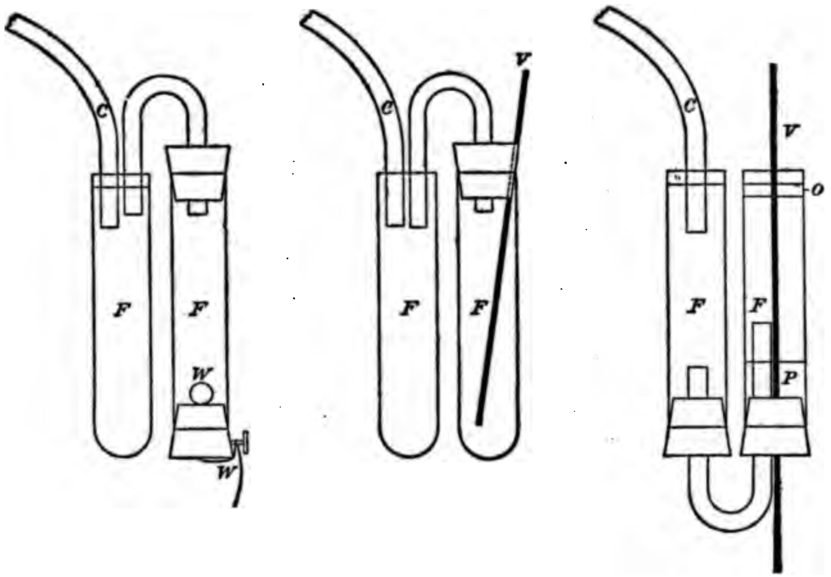

FIG. 2. FIG. 3. FIG. 4.

RECEPTACLES FOR IRON ELECTRODES.

C. Tube leading to decinormal electrode.
F. Contains normal ferrous sulphate solution.
O. Protecting layer of paraffin oil.
P. Hard paraffin.
V. Iron wire.
W. Platinum wire and loop for holding porous iron.

sulphate used was prepared by dissolving almost the necessary amount of pure crystals in a quantity of water, adding a small measured amount of sulphuric acid, and making up to a liter. Then pieces of piano wire, carefully cleaned, were added. The acid acting on the iron thoroughly reduced the solution, the amount of the acid having been so chosen that just the necessary amount of iron dissolved to make the solution normal. Several months were needed to remove the last traces of acid—an essential condition. The flask was connected with an automatic hydrogen generator whose cock was always open, and when liquid was withdrawn through the siphon hydrogen took its place. This also is represented in figure 1. Thus after having once prepared the solution, it could be kept indefinitely, perfectly constant and always at hand.

THE EFFECT OF PRESSURE.

In the following work the term "porous iron" will be used for the sake of brevity to designate the iron which had been reduced from oxide in the manner described on pages 6 and 7.

The results of a series of preliminary experiments with this porous iron are given in table 1.

The first two were made with samples which had merely suffered exposure to air. The next four had received further treatment, having been put into a small iron mortar such as is used in powdering rocks, and beaten with a heavy hammer. Under this treatment the friable, porous iron became compact and gained a shining metallic surface. The electromotive forces of these samples were then measured after immersion in normal ferrous sulphate. The cracked and powdered edges of numbers 2 and 3 were covered with shellac, so that only the smooth metallic surface was exposed to the solution.

TABLE 1.—*Preliminary experiments—Electromotive force of iron against decinormal electrode.*

Time elapsed after immersion.	Sample 1, porous iron.	Sample 2, porous iron.	Sample 3, beaten iron.	Sample 4, beaten iron,	Sample 5, beaten iron.	Sample 6, beaten iron.
Minute.	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.
1	......	......	......	0.704	0.655	0.655
2	......	......	0.674	......	......	0.685
4	0.754	0.755	......	......	......	......
20	0.780	0.774	0.724	0.720	0.674	0.722
55	......	......	0.737	0.728	0.674	0.736
240	0.801	0.799	......	......	......	......

A glance at the table shows that the beating had made considerable difference in the electromotive force of the iron in every sample which had been beaten. It will be shown later, however, that this difference was due not to the compression, but to another effect of the treatment.

This effect was soon found to be closely connected with another relation to be observed in the above figures; namely, the fact that after immersion the electromotive force of each piece of iron begins at a low point and rises, attaining constancy at a maximum only after some time. In order to study this phenomenon more closely, six other small pieces were immersed in the solution and readings of the electromotive forces taken at short intervals. The numerical results are given in table 2.

Because it was evident that the electromotive force continued to rise slowly for a very long time, four of these pieces were carefully sealed up with paraffin immediately after immersion in order to prevent oxidation. This was done in order to determine the electromotive force of the final equilibrium. After three days No. 9 and No. 10 were opened and measured; and after five days No. 11 and No. 12.

TABLE 2.—*The increase of electromotive force with time—Iron electrode against decinormal electrode.*

Time elapsed after immersion.	Sample 7.	Sample 8.	Sample 9.	Sample 10.	Sample 11.	Sample 12.
	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.
0^h 2^m	0.590	0.690	......	......	......	.....
0 2.75	0.645	0.745	......	......	......	......
0 6	0.685	0.764	......	......	......	......
0 13	0.714	0.774	......	......	......	......
0 50	0.749	0.785	......	......	......	......
73 0	......	......	0.789	0.793	......	......
78 0	......	......	0.791	0.794	......	......
119 0	......	......	......	......	0.782	0.784
120 0	......	......	......	......	0.784	0.786

This was later repeated with other samples, which gave similar results. It should be noted that after several days a pale-green precipitate of ferrous hydroxide was always found in the tube, but this seemed to exercise no considerable effect on the potential until seven or eight days had passed and the amount had become large. Even then by shaking the constant value of the potential was usually regained.

Thus it was obvious that spongy iron which has been exposed to the air always gives at first an abnormally low electromotive effect, which slowly rises. The only reasonable hypothesis capable of explaining the phenomenon seems to be the conclusion that the exposure to the air results in the formation of an exceedingly thin coating of oxide or at least of adsorbed oxygen, and that when this coating is removed, by solution or reduction, the true electromotive force is obtained.[14]

Accordingly, the iron to be used in the succeeding experiments was sealed in hydrogen. The tubes were broken open just before the samples were to be used, and their electromotive forces were measured as soon as possible afterwards. In this way the exposure to air was as short as possible and the theory was confirmed, for they were found to attain their maximum values very promptly.

With these samples a more careful study of the effect of pressure was begun. A number of preliminary experiments were made with pressures produced by 30,000 and 60,000 pounds. These pressures were quite sufficient to cause cold-welding of the particles of the porous iron, giving firm, hard plates with bright metallic surfaces. The area of these surfaces was seldom more than the half of a square centimeter, hence the pressures were approximately 30,000 to 60,000 kilograms per square centimeter. The compression was done between two smooth plates of steel in a large testing-machine in the Engineering Department of Harvard University. The pressure was great enough to press the soft iron into the steel plates, leaving distinct indentations. The iron was handled only with iron pincers. Everything with which it came in contact was kept scrupulously clean. The edges of the compressed pieces being cracked and split, they were embedded in soft paraffin before immersion in the ferrous sulphate solution, leaving exposed for measurement only the center, which had certainly borne the full effect of the pressure.

It appeared that iron thus treated gave results in no way different from the spongy pieces before compression, except that the compact specimens were slower in reaching their maxima. When reached, these maxima were essentially identical with those of the porous specimens.

Nevertheless, it seemed worth while to carry the matter further. Through the kindness of Lieutenant-Colonel J. G. Butler in charge, it was possible to subject other portions of pure spongy iron to still greater pressure on the magnificent testing machine at the United States Arsenal at Watertown, Massachusetts. This machine is capable of not only exerting a weight-effect of 1,000,000 pounds, but of measuring with great accuracy the magnitude of the effect it exerts. Two special blocks were made between which to compress the iron. In order to resist such enormous pressures they were made of the very finest tool steel, and after the lathe-work was finished they were quenched to a condition of maximum hardness. They were frustra of cones, the diameters of the bases being about 16 cm. and those of the tops, between which the iron was compressed, about 3 cm. Their heights were about 8 cm. The pressures exerted were 500,000 pounds and 700,000 pounds. Exactly how much of this pressure bore on the iron test-piece it is impossible to say, for the soft iron was pressed so deeply into the hard steel that there was some possibility of the whole top surface (7 sq. cm.) receiving part of the pressure. On the other hand, if, as is probable, the test-piece alone bore the stress, the maximum pressure was at least 350,000 kilograms per sq. cm., for the surface of the soft iron was never 1 sq. cm.

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[14] This experience, and the conclusion derived from it, agrees with that of Muttimann and Fraunberger (Sitzber. Akad. der Wiss. München, 34, 201) (1904). Their investigation was published after this part of our research had been completed, and was wholly independent.

In order to make more striking any differences which might result from these pressures, samples 13 and 14 had each been broken in two, and one piece of each was kept in a spongy condition, in order to compare with the other compressed one. Thus it was certain that all treatment previous to measurement[15] had been precisely the same, except for this one matter of compression. Other pieces of porous iron gave essentially the same results.

As in the previous experiments, the edges of the compressed iron were protected with paraffin, so that the exposed surface should be that alone which had been compressed.

TABLE 3.—*The effect of previous compression on the electromotive force—Iron electrode against decinormal electrode.*

Time elapsed after immersion.	Sample 13, porous.	Sample 13 after subjection to 250,000 kg. pressure.	Sample 14, porous.	Sample 14 after subjection to 350,000 kg. pressure.	Sample 15 after subjection to 350,000 kg. pressure.	Sample 16 after subjection to 350,000 kg. pressure.
	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.
0h 11m	......	......	......	0.781	.....	0.722
0 28	0.775	0.755	0.786	......	0.744	......
6 0	0.781	0.781	0.787	0.770	0.783	0.750
21 0	0.780	0.782	0.787	0.782	0.788	0.751

The results with samples 13 to 15, inclusive, lead to the conclusion that no permanent change in free energy had resulted from the compression. They are exactly similar to those obtained with the lower pressures. The apparently contradictory result of sample 16 will be shortly explained.

As a step toward this explanation, it is necessary to call attention once more to the fact that the compressed pieces at first yielded too low an electromotive force, although the value afterwards rose to equal that of the uncompressed pieces. An explanation for these low values is to be found in the idea already mentioned on page 13, there advanced to explain the lag of porous iron which had been kept for some time in a desiccator. It is that an exceedingly thin coating of oxide is formed on the iron by exposure to the air and thus the true electromotive force is masked until this coating is dissolved. Most of the samples of porous iron had been kept a whole day in a desiccator after reduction before immersion, while sample 14 in table 3 had been kept only three hours. The difference in the speed of attaining the maximum value is very marked. This theory not only seems to account for the effect of long exposure to air, but also offers a simple explanation for the slightly lower initial potential of the compressed samples. The length of time during which the compressed pieces were exposed to the air before measurement was exactly the same as that of the parallel porous ones, but the former were inevitably heated somewhat in the act of compression, and thus an oxide coating might well have been formed which would equal in effect one of long, slow formation in a desiccator. The theory probably also offers the most satisfactory explanation of the exaggerated deficiency exhibited by No. 16 in table 3. The blocks between which No. 16 was compressed had been three times subjected to such enormous pressures that they were beginning to fail, and this fourth and last time the blocks split with bright sparks and loud reports, and threw small pieces in all directions. Under such treatment the blocks undoubtedly became warm, and it is quite to be expected that this last sample should possess the heaviest and firmest coating of oxide.

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[15] Including the temperature to which it had been exposed, the importance of which will shortly be pointed out.

Thus it is fairly safe to conclude that even such enormous pressures as 300,000 kilograms per square centimeter produce no permanent change of free energy in iron.

It is interesting to compare this constancy with the behavior of other properties of metals on subjection to great stress. Since this work was done, Dr. Stull and one of us has found, in the work already referred to, that after subjection to pressures up to 500 atmospheres all of thirty-odd elements examined regain precisely the original volume. The method used is unique and allows of the detection of volume changes of 0.000,01 milliliter in a sample of 10 milliliters.

After this work was done we became acquainted with two pertinent papers by W. Spring,[18] in which he proves the same fact by still another method, the one, in fact, which would most naturally be adopted if that were the main object of the research, namely, the determining of the specific gravity before and after compression. He first submitted to pressures up to 10,000 atmospheres more than eighty solids of the most diverse chemical nature, and found that powders weld together perfectly under pressure, as we found with iron. In order to do this, he found it necessary to compress in a vacuum, because imprisoned air not only prevented contact of the particles, but also tore them apart again when pressure was released. All of his work was performed with the care which this precaution indicates. The result of one investigation, entitled "L'élasticité parfaite des corps chimiquement définis," is best given in his own words:

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[18] Bull. Acad. Roy. de Belg. (3), 6, 509 (1883); Ibid. (1903), p. 1066.

> La plupart des corps examinés ont manifesté une petite augmentation permanente de densité après avoir subi une pression d'environ 20,000 atmosphères, mais, celle-ci une fois réalisée, ils ont résisté opionâtrément à toute diminution permanente ultérieure de leur volume. Pour tous la densité a atteint bientôt *un maximum*. La faible augmentation de densité permanente observée n'a cependant jamais eu pour cause une contraction réelle de la matière. Toujours elle a été due à l'écrasement, par pression, des cavités existant d'avance dans le corps examiné, ou bien à la disparition de fissures plus ou moins évidentes. En un mot, on s'est trouvé en présence d'un fait accidentel, pouvant facilement amener une erreur, mais non d'un phénomène physique essentiel.

Thus the present work on the electromotive force of iron subjected to great stress confirms the very different work of Spring on densities. In so far as these data show that when no change of specific gravity is effected by a given application of energy, no change in the free energy of the system results, they support the theory of compressible atoms.

TENSION EXPERIMENTS.

Although it thus appears to be impossible to produce permanent free energy changes in pure iron through pressure alone, it appeared possible that measurements of electromotive force made while the metal was under tensile stress might show varying values, because tension produces marked physical changes in the metal. These changes are as follows: (1) A strain which immediately disappears on release of the tension, inside the elastic limit. (2) Beyond the elastic limit a permanent strain, with increasing stress needed to produce equal increment of strain, up to the ultimate resistance. (3) Beyond the ultimate resistance, with ductile metals, there is a region before the actual break occurs, where, for increase of strain, decreasing stress is required, until failure takes place. It seemed reasonable to expect that such decided and sudden changes in the cohesion would be accompanied by free-energy changes.

While under stress, or after a "permanent set" has been produced by strain beyond the elastic limit, the iron is in unstable equilibrium. Sufficient proof that it is so within the elastic limit lies in the fact that it returns of itself to its original dimensions. Beyond the elastic limit, the custom in wire manufacture, of returning the wire perhaps half a dozen times to the annealing pots to be softened, speaks for itself. By heating to 300° to 400° for several hours " the molecular tension in the wire caused by drawing " is released.[17] The molecules, given the opportunity through increased mobility at higher temperatures, may be supposed to return to their normal relations to each other and plasticity is restored to the iron.

Further evidence in this direction is furnished by a piece of work done by Barus, entitled " The Energy Potentialized in Permanent Changes of Molecular Configuration."[18] He pulled wires of various metals to the point of failure, determined their rise in temperature by means of a thermopile, and subtracting the heat evolved from the total work done on the wires, obtained values for the amounts of energy which had become potential in the metals. He says:

> To summarize, it appears that as much as one-half of the work done in stretching up to the limit of rupture may be stored up permanently; that the amount of work thermally dissipated varies considerably with the metal acted upon, being very large, for instance, in copper (75 per cent) and smaller in the case of iron (50 per cent); that in the case of the same given metal the work is largely potentialized during incipient stages of strain, and very largely dissipated during final stages of strain. When stress of a given kind is applied to different metals, the total amount of energy which can be stored per unit section, per unit of length up to the limits of rupture, may therefore be looked upon as a molecular constant of the metal.

In a table he gives results showing that in an iron wire of 0.136 cm. diameter, stretched almost to the limit of rupture, at least 2 megergs per centimeter are potentialized, about the same amount having been dissipated as heat. Knowing this value, it is possible to calculate the maximum rise in electromotive force theoretically required by such an increase in the free energy of the metal, supposing that all this work were available as free energy. The general formula for such a calculation is:

$$\Delta\pi = \frac{WE}{96580m}$$

in which

$W =$ the work in joules done per centimeter of the wire;
$E =$ the electrochemical equivalent of the metal, in grams;
$m =$ the weight of the metal per centimeter of wire; and
$W \times E/m =$ the work done per gram equivalent of the metal.

Substituting values found by Barus, we have:

$$\Delta\pi = 0.432 \times 27.95/0.1114 \times 1/96580 = 0.0011 \text{ volt.}$$

(The radius of the wire was 0.068 cm. and its density 7.68.)

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[17] " Wire, its Manufacture and Uses," J. B. Smith, pp. 30, 54, and 56.

[18] Amer. Journ. Sci. (3), 38, 193 (1889); also U. S. Geological Survey Bulletin No. 94, p. 101 (1892).

[illegible]

[illegible]

[illegible]

[illegible]

PRELIMINARY EXPERIMENTS

[illegible] responsible for the great [illegible] energy change [illegible] it appeared possible that [illegible] when the metal was under tensile [illegible] marked physical change in the metal. These changes are as follows: (1) A strain which is [illegible] of the [illegible] inside the elastic limit; (2) Beyond the elastic limit a permanent strain, with increasing stress [illegible] to produce equal increment of strain up to the ultimate resistance; (3) Beyond the ultimate resistance, with ductile metals, there is a region before the actual break occurs where for increase of strain, decreasing stress is required until failure takes place. It seemed reasonable to expect that such decided and sudden changes in the cohesion would be accompanied by the energy changes.

While under stress or after a "permanent set" has been produced by strain beyond the elastic limit the iron is in unstable equilibrium. Sufficient proof that it is so within the elastic limit lies in the fact that it returns to

Two other calculations will be given to illustrate more fully the changes to be expected. The data for these were found in a book[19] which is still quoted as an authority by engineers, although published as long ago as 1879.

In the first of these (p. 24) the test-pieces were taken "from a bar of remarkably pure, refined, and uniform iron." The average of nine tests, very uniform in their results, gave: Breaking stress per square inch, 55,489 pounds; elongation, 23.9 per cent. The diameters of the test-pieces were 0.974 inch. Calculating as before, we get 0.0034 volt as the change to be expected.

In the second one the iron is described as "very soft and ductile." The average of four tests gave: Stress per square inch, 45,873 pounds; elongation, 29.7 per cent. The diameters were 1.000 inch. These data give 0.0035 volt as the expected rise.

The results of all these calculations should be divided by 2, since Barus showed that only 50 per cent of the work done becomes potential. These calculated values, never exceeding 1.8 millivolts, represent the maximum values for the increase of potential—values which may not be actually attained, because it is by no means certain that all the energy thus stored is available as free energy. Moreover, the distribution of the strain between surface and interior is uncertain. This is indicated by the following statement of Burr:[20]

> It has been found by experiment that bars of wrought iron which are apparently precisely alike in every respect, except in area of normal section, *do not give the same ultimate tensile resistance per square inch.* Other things being the same, *bars of the smallest cross section give the greatest intensity of ultimate tensile resistance.*

This is due to the fact that shearing strains increase with greater cross section. And also,[21]

> If the tensile stress is uniformly distributed over each end of the test-piece, it will not be so distributed over any other normal section. Since lateral contraction takes place, the exterior molecules of the piece must move toward the center; but if this motion exists, the molecules in the vicinity of the center must be drawn farther apart, or suffer greater strains, than those near the surface. Hence the stress will no longer be uniformly distributed, but the greatest intensity will exist at the center and the least at the surface of the piece. These effects will evidently increase, with a given form of cross section, with the area.

Smith,[22] in pointing out the strengthening effect of drawing wire has said: "In the case of the wire drawn through three holes the tenacity of the metal was increased 95 per cent above that of the billet;" and Burr says:[a] "Wire is the strongest form in which iron can be used to resist tensile stress."

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[19] "Experiments on the strength of wrought iron." Report of the Committee of the United States board appointed to test iron, steel, and other metals. Commander L. A. Beardslee, U. S. N. Abridged by William Kent. New York, 1879.

[20] Elasticity and resistance of the materials of engineering, p. 218. New York, 1903.

[21] Ibid., p. 206.

[22] "Wire, its manufacture and uses," p. 58.

It is evident, then, that by pulling a wire of small cross-sectional area it is possible to exert the maximum of stress on the surface of a test-piece.

The apparatus (shown in figure 4, page 10) employed in our experiments was exceedingly simple. The upper end of the wire was twisted around an iron support and the pull was exerted by weights in a basket attached to the lower end. In the middle the wire was narrowed at one place, and this was surrounded by a tube of normal ferrous sulphate and connected with a normal calomel electrode. The results were at first highly irregular. The electromotive force of the wires used (pure piano wire and pure soft iron wire) varied over a range of 0.005 volt without apparent cause. Merely tapping the stretched wire sometimes caused a momentary rise of from 0.003 to 0.004 volt. Such electrical disturbances from mechanical jarring have been observed by von Helmholtz. In one case the addition of 5 kilograms to the load caused a net rise of about 0.0007 volt and the next 5 brought it down again by the same amount, while one more brought it up again by 0.0005.

Calculating the theoretical change of potential, we get 0.0017 volt for the total work done, and half of this, or 0.0009 volt, as the change to be expected according to Barus. The data for this calculation are: Tensile strength, 25 kilograms; elongation, 9.3 per cent; diameter of wire, 0.08 cm.

Hence the accidental disturbances exceeded the maximum theoretical effect and entirely masked the latter.

Only one regularity was noticeable, namely, that at the instant at which the load was increased there was a momentary drop in electromotive force. Starting with no load at all and the potentiometer reading 0.7145 volt,[aa] a 10 kg. load was applied, and at the same instant the galvanometer swung 18 to 20 divisions to the right, and then instantly swung back again very rapidly to the permanent reading, 0.7125 volt. Exactly how much fall of potential this swing to the right indicates could be determined only with a ballistic galvanometer, but it may have been as much as 0.015 volt. The addition of another kilogram had a similar effect, except that the swing was only 12 to 15 divisions to the right and it returned more slowly to 0.7125. The third 10 kg. caused a smaller swing still, and a much slower return to 0.7125. About that value was always reached after standing a few minutes.

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[a] Elasticity and resistance of the materials of engineering, p. 241.

[aa] This reading, being taken with the help of a *normal* calomel electrode, must have 0.052 volt added to it in order to be comparable with the other potentials recorded in the paper. It thus becomes 0.766, the same as before. The normal electrode has less resistance and allows more sensitive readings than the decinormal.

The weights were then added to 48 kg., the last ten still causing a slight swing to the right. A 13 kg. weight was then added to the load, and the wire lengthened rapidly and would have undoubtedly broken had not the support stopped the basket. The galvanometer swung 8.5 divisions to the *left,* indicating a *rise* of about 0.004 volt, and quickly swung back again.

These temporary changes and the change in sign which they undergo are highly interesting. The most obvious explanation of the first effect of diminished potential is to ascribe this to heating incidental to pulling, and experiment gave the idea some support. Heating the wire to redness with a small gas flame just above the surface of the liquid gave a somewhat variable electromotive force, the mean value being about 0.015 volt *below* the initial one—an effect about like the first effect noted above. When cold the wire returned to the initial value. This is advanced as a suggestion rather than a definitive explanation, however.

The decreasing temperature effect due to the successive additional stresses may have been due to the larger percentage of storing as potential energy as the elastic limit is approached—and the final excess of potential may have been due to the sudden manifestation of this increased potential at the point of fracture.

Nevertheless, these conclusions are highly hypothetical. The results do not permit of conclusions broader or more definite than these. On the other hand, they afford the opportunity of correcting two pieces of work which have been widely published and whose incorrect results have been given general credence. The subject is of such great importance to modern engineering that, naturally enough, engineers were the ones attracted to its investigation. M. P. Wood, in his book "Rustless Coatings; Corrosion and Electrolysis of Iron and Steel,"[25] under the heading "Corrosion Increased by Stress" (p. 348), quotes three men as entitled to a hearing on this subject.

The first of these, Thomas Andrews,[26] carried out experiments far from satisfactory from the electrochemical point of view, because he used a solution of common salt as an electrolyte, and prepared the two pieces of iron for comparison in different ways. The observed difference in potential is quite as probably to be ascribed to the oxidation effect already discussed as to the effect of strain, although a part of the effect may have been due to strain.

The second paper quoted by Wood is "An Experimental Study of the Corrosion of Iron under Different Conditions," by Carl Hambuechen.[27] Of this paper the section on "Corrosion of Strained Metal," which is the only part to be discussed here, is no more conclusive than Andrews's work, although Hambuechen states his conclusions in unqualified terms. The work was very carefully performed in every particular except one, namely, the fact that he chose ferric chloride solution as the electrolyte in which to measure the electromotive force of the iron test-pieces. This unfortunate choice completely invalidates all the results. The reason is very simple. Ferric chloride is always hydrolyzed to a considerable extent—that is, it contains acid. When such a solution comes in contact with iron the three following reactions take place:

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[25] Wiley & Sons, N. Y., 1904.

[26] Proc. Inst. Civil. Engin. 118, 356-374 (1894).

[27] Trans. Amer. Soc. Mechan. Engin., 22, 816-821 (1901); or Bull. Univ. Wisconsin, Engin. Series, vol. 2, No. 8, (1900).

$$\mathrm{Fe} + 2\mathrm{Fe}^{+++} = 3\mathrm{Fe}^{++} \text{ (or } \mathrm{Fe} + 2\mathrm{FeCl}_3 = 3\mathrm{FeCl}_2\text{).}$$
$$\mathrm{Fe} + 2\mathrm{H}^{+} = \mathrm{Fe}^{++} + \mathrm{H}_2 \text{ (or } 2\mathrm{HCl} + \mathrm{Fe} = \mathrm{FeCl}_2 + \mathrm{H}_2\text{).}$$
$$\mathrm{H} \text{ (nascent) } + \mathrm{Fe}^{+++} = \mathrm{Fe}^{++} + \mathrm{H}^{+} \text{ (or } \mathrm{H} + \mathrm{FeCl}_3 = \mathrm{FeCl}_2 + \mathrm{HCl}\text{).}$$

There exists, then, at the electrode a continually changing concentration of ferric, ferrous, and hydrogen ions, and reliable work is out of the question. The effect of all these influences combined would cause the electromotive force to change steadily, quite independently of any stress and strain effects. The rate of this change would depend on such indeterminate and chance relations as the area of the iron surface to the volume and the concentration of the solution, and on the mechanical arrangement, allowing more or less rapid diffusion, etc. The following experiments are enough to show this. Wires of pure iron were cleaned with fine emery cloth, carefully wiped, and simply immersed in a ferric chloride solution.[*] They were under no artificial strain of any kind when measured.

TABLE 4.—*The electromotive force of iron in ferric chloride against the decinormal electrode.*

Piano wire (20).		Soft wire (21).	
Elapsed time.	E. M. F.	Elapsed time,	E. M. F.
	Volt.		Volt.
0^h 0.5^m	0.550	0^h 1^m	0.595
0 5	0.5725	0 5	0.608
0 10	0.576	0 10	0.610
0 30	0.585	0 15	0.610
0 40	0.588	15 55	0.718
17 0	0.743	16 40	0.716

During the first day hydrogen was steadily evolved from both wires, but the second day this side reaction was greatly diminished. As is seen in the table, the electromotive forces rose in these cases respectively 0.192 and 0.123

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[*] Similar results were found by Finkelstein in 1902. (Z. phys. Chem., 39, 91).

volt. This rise would have been ascribed by Hambuechen to strain. Further experiment could add nothing to the argument. It will be noticed that even finally the potential was very far from the value in ferrous sulphate, 0.765.

Hambuechen's results are quite as irregular, as one would infer from these considerations. For example, the change in electromotive force, caused supposedly by tensile stress, varies in two cases from 0.004 to 0.056 volt, and yet in the former case the load per square inch was actually 600 pounds greater than in the latter. Hambuechen realized that some of his observed potentials were much larger than were to be expected, and therefore explained that "One of the assumptions it was necessary to make is that the stress equally affected the entire cross section, which is by no means the case, for it is the outside layer which is affected the most and would therefore give higher values of electromotive force than the calculated amounts." This is exactly the opposite assumption to that demanded by the reasonable explanation of Burr already quoted (p. 18).

From the theoretical point of view, the matter appears, then, to be more complicated than might be inferred from a hasty survey of it. One can not safely conclude that the potential on the surface of a wire is an index of the free-energy change in the interior of the wire; and one can not assume that the electrochemical behavior of wire while under stress is the same as when the stress is removed. Still further, one can not but believe that the permanent strain caused by a stress (that is to say, the energy potentialized by a stress) will differ in the case of impure iron from that in the case of pure iron. Moreover, it is by no means certain that energy stored in iron by change of internal structure is available as free energy.

Taking all these considerations together, and weighing also the electrochemical defects in some of the papers just discussed, it is apparent that none of these investigations furnish conclusive evidence concerning the magnitude of the changes of potential to be noticed on stretching a rod or wire. It is apparent, moreover, that this change is smaller than is usually supposed, although it is probable that a slight change of electromotive force is caused by a tensile strain of impure iron.

Qualitative evidence on this point is furnished by a paper entitled "The Effect of Strain on the Rate of Solution of Steel," published by Barus in the Bulletin 94 of the U. S. Geological Survey (p. 61), already quoted. He experimented with soft steel, hard-drawn steel, and the latter annealed; he determined the rate of solution by loss of weight, and he concluded his report as follows: "Summarizing the above results as a whole, it follows that the rate of solution of drawn steel is greater than the rate of the same homogeneous metal similarly circumstanced." In applying the results it should be noted that steel alone, not pure iron, was experimented upon; that any speed of reaction in which two phases are involved is complicated by many disturbing factors; and that the tendency of iron to occlude hydrogen, discussed in a later section of this paper, must have added another complication.[a]

Because our results obtained by applying both compressing and distending stresses upon pure iron had been chiefly negative, indicating very slight changes of free energy for large stresses, attention was now directed to the change of the other conditions of experiment, with the hope of tracing to these other conditions the fairly large changes of electromotive force actually to be observed in specimens of pure iron prepared in different ways.

THE EFFECT OF VARYING THE TEMPERATURE OF IGNITION.

It will be noticed on studying tables 2 and 3 that the electromotive forces of cells made from different samples of iron which were chemically alike varied between such wide limits as 0.780 to 0.794 volt, a range far beyond the limits of experimental error.

In tracing these differences back to their fundamental cause, the first clue was furnished by the different degrees of cohesion or compactness exhibited by the several specimens. When the four pieces of porous iron, the results from which are given in table 3, were removed from the cells at the completion of the electrochemical experiments, they were examined with regard to their cohesion by the simple method of resistance to pressure and to fracture between the fingers. It was thus found that No. 2 iron felt softest, No. 3 the hardest and firmest, and Nos. 1 and 4 somewhere between. Reference to the table shows that No. 2 had the highest electromotive force and No. 3 the lowest; hence a more powdery structure evidently went with greater tendency to dissolve. Repetition with other samples confirmed this view.

What, now, could be the cause of this difference in compactness of the different samples? It is well known that many substances, on being heated, begin to cohere at temperatures far below their melting-points, exhibiting the shrinkage commonly called "sintering." It is also well known that this effect becomes more and more noticeable as the melting-point is approached. Probably, then, these different samples had been subjected to different temperatures during their reduction. This relationship was easily confirmed by further experiment. Iron reduced at high temperatures was found to be far firmer in structure than that reduced at low temperatures. In order thus to find the highest potential attainable in this way, iron should obviously be reduced at the lowest possible temperature. Accordingly two samples were prepared, the first being very slowly reduced at a temperature well below 800°. In the second of these reductions the temperature was measured by a Le Chatelier thermopile laid under the boat containing the iron, and the highest temperature it indicated through a reduction lasting three days was 615°. The iron in boat No. 1 was of a clear gray color in those parts where the temperature became highest and dark blackish gray on the surface. All the iron in boat No. 2 was like the top of boat No. 1. Even the firmest iron in boat No. 1 could easily be crushed between the fingers.

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[a] In this connection attention is called to the interesting work of C. S. Burgess on the effect of impurities on the rate of solution, read at the recent meeting of the American Electrochemical Society, May, 1906.

Two samples of the light-gray material from boat No. 1 gave the following measurements:

TABLE 5.—*The electromotive force of porous iron reduced at low temperature.*

Sample 22.		Sample 23.	
Elapsed time.	E. M. F.	Elapsed time.	E. M. F.
	Volt.		Volt.
0^h 8^m	0.796	0^h 14^m	0.797
0 30	0.800	1 0	0.797
1 0	0.798	24 5	0.799
24 0	0.799	70 40	0.800
70 10	0.796	92 0	0.800

These values are somewhat higher (0.002 and 0.006 volt) than any obtained in previous work, and are further evidence in favor of believing that the low temperature of reduction really causes a product having a higher potential. The contents of boat No. 2 were found to contain much hydrogen, and will be discussed later.

Having thus shown that iron reduced at low temperature may give in combination with the decinormal electrode a potential as high as 0.800 volt, and that increasing temperature of reduction causes a steady decrease in this value until the metal prepared at perhaps 1,200° gives a value as low as 0.776, it became a matter of interest to discover if iron subjected to a still higher temperature might not give a still lower value. The obvious subsequent step was therefore to test iron which had been fused, and accordingly several specimens of the purest commercial iron (Swedish bar iron and pure piano wire) were tested in preliminary experiments. The Swedish bar iron was very pure, and soon reached a constant value. The piano wire was less regular, and hence was examined more thoroughly. The wire was "hard drawn," and its purity was indicated by the fact that when heated to 1,000° in hydrogen and quenched in ice-water it was as soft and pliable as the purest iron. Two pieces of this wire were scraped bright and clean with a dull knife and measured as usual in a cell shown in figure 3, page 10. The potential of these cells began at very low value, and gradually rose to a constancy at about 0.76 volt. It was evident that the end-point is reached only after a long time; and accordingly six wires were sealed up in ferrous sulphate solution. Three of these had been scraped as before to clean them and the other three were rubbed with fine emery cloth, all of them being carefully wiped with a cloth before immersion. Below are given the final constant values attained by these samples:

Table 6.—*The electromotive force of commercial iron of moderate purity.*

Elapsed time.	Swedish bar iron.	Piano wire (hard drawn).					
		Sandpapered.			Scraped.		
	No. 24.	No. 25.	No. 26.	No. 27.	No. 28.	No. 29.	No. 30.
	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.
3 hours....	0.765	......	......	......	......	......	......
1 day......	0.770	......	......	......	......	......	......
3 days.....	0.770	0.762	0.762	0.762	0.767	0.769	0.765
4 days.....	......	0.762	0.762	0.762	0.763	0.767	0.765
7 days.....	......	0.762	0.763	0.763	0.765	0.767	0.763

Thus all these samples yield a result lower than the most compact of the sintered samples. The results show excellent agreement, and the number 0.765 volt may be taken as the true electromotive force of the cell made from this wire. The Swedish iron gave a slightly higher value, about 0.770. A third sample of commercial iron, the softest and purest wire obtainable, was next examined. It was cleaned with fine emery cloth and wiped with a clean cotton cloth. Two specimens after two days gave respectively 0.760 and 0.771 volt, or in mean 0.766, essentially the same as before.

Thus all the commercial compact samples of iron showed a distinctly lower solution tension than any of the spongy pure samples. Before this difference could be certainly ascribed to any peculiarity in the freshly reduced spongy iron, proof must be afforded that it was not due to impurities in the commercial samples. This possibility was most conveniently subjected to trial by fusing a sample of pure reduced iron, and comparing the product with the commercial sample. At first an attempt was made to prepare pure fused iron by fusing a small quantity in a small lime crucible in an oxyhydrogen flame. The hydrogen used was very pure, having been made by electrolysis, for impurities would be taken from the gas by the fused iron. The flame was so directed as to cover the iron completely and was provided with excess of hydrogen, but nevertheless all the iron oxidized. The oxide unfortunately did not act as a protection to the iron underneath, because it fused and was absorbed by the porous lime. No acceptable variations of apparatus or manipulation greatly bettered the result, which could have been easily accomplished with larger quantities of material. Therefore another method was tried, namely, the melting of the iron in a vacuum by means of the heat generated by its own resistance to a great electric current. Besides an apparatus suitable for exhaustion, the essentials for success were iron electrodes, a suitable crucible, and a sufficiently high current. Bundles of piano wire provided the electrodes, and a nest of powdered iron, supported on a crucible of lime made from the purest marble, was used to contain the melted particles. In order to increase the resistance of the metal it was powdered in the Hempel steel mortar, and the current was passed through this powder. The arrangement of the apparatus and its description are given in figure 5.

The operation of the experiment was as follows: After everything was arranged as shown in the figure, the Sprengel vacuum-pump was started and the stoppers thus firmly forced in. This, however, disarranged the electrodes and air was again admitted, so that they could be carefully placed at the desired places in the lime boat. The apparatus was now evacuated a second time and the current turned on. For some time nothing happened, but finally the metal fused with the help of vigorous jarring. More and more powder was added from above as the fusion progressed. There were brilliant flashes of violet light with each addition of powder, followed by bright-red glowing. By feeding powder into the open spaces left by the fused material it was possible to maintain the fusion almost continually until the supply was exhausted. The product consisted mainly of small pellets about the size of the head of a pin or a little larger, resting in the nests of pure powdered iron. Only one was large enough to use conveniently in a cell. Nevertheless, this gave a result agreeing so well with that from the commercial materials that a duplicate seemed unnecessary. The sample was covered with soft paraffin on those parts which did not have a smooth fused surface.

Table 7.—*Pure iron fused in vacuum.* (33).

Elapsed time.	E. M. F.	Elapsed time.	E. M. F.
	Volt.		Volt.
0^h 7^m	0.745	40^h 40^m	0.761
0 9	0.750	41 30	0.759
0 20	0.757	72 10	0.763
0 40	0.760	90 25	0.761

Thus this sample of exceedingly pure iron fused in vacuum gave essentially the same potential as good quality commercial material (0.765).

This iron must have been wholly free from carbon, from any other metal, and indeed even from all but the merest trace of hydrogen. It is hence clear that the impurities in the commercial iron could not have been enough to affect its electromotive force, and that pure, compact iron really gives a lower value than the same iron reduced by hydrogen. To what cause, then, is this difference to be ascribed? Is the higher solution tension of the spongy iron due to the traces of hydrogen within it, or to difference of internal structure, or to the disposal of its external surface?

The first of these three possible causes of an extraordinarily high potential does not seem to be a very probable one; nevertheless, it seemed worthy of test, especially in view of the results on occluded hydrogen to be recorded later. Accordingly, several samples of spongy iron were ignited for varying lengths of time at varying temperatures in a vacuum, while inclosed in a stout porcelain tube. It was thus found that while short ignition or ignition at a low temperature left much of the gas in the metal, treatment at a higher temperature for a longer time seemed to remove nearly all of it, while causing the iron to sinter into a compact mass. Iron thus treated at 1,160° gave in conjunction with the decinormal electrode the usual potential 0.787 in a few hours, a value which remained unchanged even in the last decimal place after ninety hours. Even this iron, however, undoubtedly contained traces of hydrogen, although much less than at first.

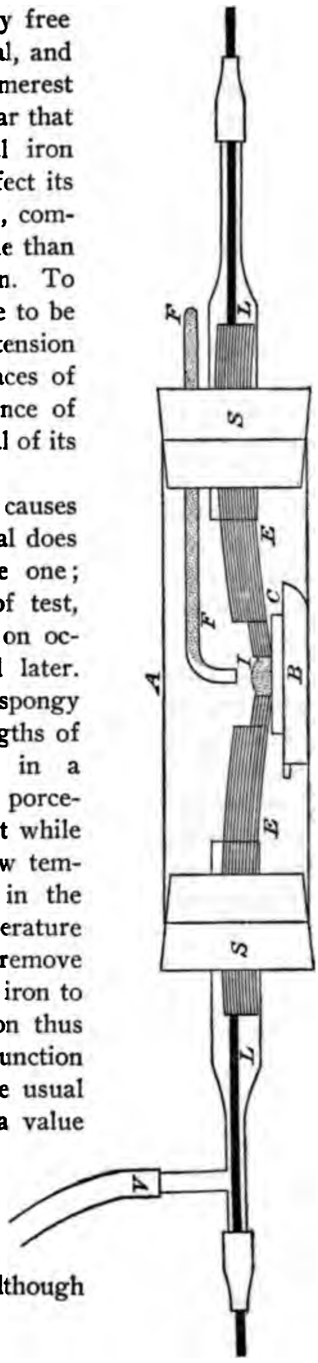

FIG. 5.—APPARATUS FOR FUSING IRON IN VACUUM.

A. Lamp chimney.
V. Tube to vacuum pump.
L, L'. Leads to dynamo.
E, E'. Piano-wire electrodes.
S, S'. Rubber stoppers (these were protected by several thicknesses of asbestos board).
B. Porcelain boat.
C. Lime crucible.
I. Iron powder to be fused.
F. Feed, glass tube filled with powder, operated by jarring.
Scale about one-third natural size.

The permanence in the value in the potential is in itself the best evidence that the hydrogen, even if present, is so shielded from the electrolyte as not to affect the measurement of electromotive force. It is improbable that a trace of occluded gas could exercise a lasting effect in maintaining the potential above that of the reversible electrode of iron in its sulphate. This matter will be discussed in detail in the second section of the paper.

There are two other hypotheses capable of explaining the abnormal potential of the spongy iron. It is certain that the "sintering' is increased and the surface of the iron diminished in this way; and it is possible that change in the degree of polymerization of the iron, resulting in the formation of a more stable modification, is likewise effected.[a] Either of these changes might affect the electromotive force. A method of deciding between these two would demand either the formation of compact iron at low temperature, or else of loose spongy iron at high temperature—and neither is capable of certain preparation. The former was nearly obtained in the experiment first recounted, in which the spongy iron was rendered compact by great pressure; the latter can hardly be obtained by mechanical subdivision.

It is to be noticed that of the first three specimens used in the experiments recorded in table 3, the untouched porous pieces gave an average potential of 0.783, while the same pieces after cold-welding at very high pressure gave the essentially identical value 0.782. The cold-welded pieces were very hard and tenacious, and appeared qualitatively in every way similar to iron which had been fused (which gave only 0.765 volt); but it is not certain that some particles on the surface were not as loosely coherent as in the sponge, and hence capable of giving as high a potential. It is true that one fact militates against this possibility—the fact, namely, that the compressed pieces steadily rose to the maximum potential and staid there a long time, which could have hardly been the case if the high potential had depended upon a few particles.

Because of the experimental difficulties it is impossible now to decide definitely between these possible causes of difference between the spongy and compact metal. It is possible that all three are superposed; but of the three, the writers are rather inclined to believe that the chief cause is probably the state of subdivision—the very finely divided particles giving a higher electromotive force than the fused mass.[a] If this is true, the case is one of great interest because of the magnitude of the effect, corresponding as it does to a tenfold greater solubility of the finest particles.

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[a] The allotropic theory of iron need not be discussed here. It has satisfactorily explained so many phenomena and has had such wide usefulness that it is universally accepted by scientific metallurgists. Its theoretical side from the standpoint of the phase rule is thoroughly treated by Roozeboom, Z. f. Phys., ch., **34**, 436 (1900). The metallurgist's use of it is shown by Baron von Jüptner in his work "Grundzüge der Siderologie," vol. 2, 1901. See also Berichte der d. Chem. Gesell., **39**, 2381 (1906).

A short explanation of the terminology may not be out of place. Pure iron has at least two well-defined transition points. Iron stable below 766° is known as alpha iron, between 766° and 895° as beta iron; and the phase formed above 895° is called gamma iron.

In this connection it was deemed worth while to test the electromotive force of iron which had been suddenly cooled or quenched. In this way it might be found whether or not pure iron, when suddenly cooled, could be caught in a condition of internal structure less stable than when cooled slowly.

Preliminary experiments, to be recounted later in another connection, showed that in order to obtain significant results for this purpose the heating and sudden cooling must occur in the absence of any foreign substance capable of reacting upon the iron; therefore the metal must be quenched in the absence of any gas or water.

The apparatus needed was not complex. A stout tube of Berlin porcelain was clamped in a vertical position, closed at both ends by Hempel water-cooled stoppers, and was heated in the middle by an encompassing perforated Fletcher furnace. The temperature was registered by a platinum-rhodium thermopile. The porcelain plate on which the test-pieces of iron were laid was suspended in the middle of the tube by an iron wire on one side and a small silver wire on the other. On the lower Hempel stopper lay a smooth, thick iron plate, and ice-cold water was circulated through the stopper, while the whole lower end of the tube was packed in ice. The apparatus was now evacuated with a Sprengel mercury pump, and when the pressure had fallen to less than 1 mm. the tube was heated. For ten minutes the temperature was kept above 1,000°; the silver wire was melted and one side of the porcelain plate was dropped. The iron of course fell from this region of high temperature to the cold iron plate. The apparatus was left to cool over night, without the admission of a trace of air. The two pieces of iron when put in had been blackish-gray and very loosely knit together; when taken out they were quite cohesive and of a clear-gray color, exactly resembling iron which had been reduced in hydrogen above 700°. This illustrates the effect of sintering and proves that the original dark color of the iron powder was not due to incomplete reduction, but solely to its state of division. One surface of one of the two pieces was found lying flat on the cold iron plate and this one was immersed in ferrous sulphate and measured. It gave in eight minutes a potential of 0.788, which slowly rose to 0.805 in an hour, and then settled down to constancy at the value of 0.795.

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[a] Ostwald, Zeitschr. für Phys. Chem., **34**, 45 (1900); Hulett, ibid., **37**, 385 (1901).

In repeating the experiment two improvements were introduced. For fear that some silver might have volatilized and contaminated the iron, the silver-wire support was replaced by a simple mechanical device, one side of the porcelain plate supporting the iron being held in place by a pipe-stem, while the other side was attached to an iron wire running through a lubricated hole in the stopper. By pulling the wire the iron could be dropped. Furthermore, quick and effectual cooling was obtained by surrounding the outside of the base of the porcelain tube, containing the iron cooling-plate, by a mixture of chloroform and solid carbon dioxide. Time was allowed for the thorough cooling of the inclosed iron plate. The temperature of porous iron was thus almost instantaneously lowered from 1,100° to —75° or thereabouts. Great pains was taken to exclude the vapor of water, which would have condensed in the cold part of the tube and vitiated the experiment. This was accomplished by running a stream of pure dry hydrogen through the tube for many hours.

As soon as possible after the fall of the porous iron, which took place this time in an atmosphere of hydrogen, the pieces were taken out, immersed in ferrous sulphate, and measured in the usual way. In six minutes after immersion the potential was 0.790, in twenty minutes 0.796, and in an hour 0.798. After a day it settled down to perfect constancy at 0.793 volt, essentially identical with the result of the previous experiment. This is not enough above the usual value (0.787) obtained from iron slowly cooled from the same high temperature to allow the conclusion that the sudden cooling had made any considerable difference in the potential or difference in internal structure.

It becomes now an interesting question as to which of the many values for the gradually changing potential of the cell Fe, $n\text{FeSO}_4$, $n/10\text{KCl}$, HgCl, Hg correspond to the true values of the solution tension of the different forms of iron. Consideration shows that the final high values are probably to be taken in each case, for several reasons. In the first place, these values are approached asymtotically, and are then maintained at a constancy for a long time. For example, one sample of iron which in 16 hours had given in the cell a potential of 0.793 volt, after 150 hours more was still practically unchanged at 0.792 volt. In the next place, the different kinds of iron, although sometimes beginning at impossibly low values, all finally rise to nearly the same point. Again, it is not conceivable that the iron should gradually raise itself to a potential above its true value and maintain itself there in a reversible reaction with a large excess of both iron and ferrous sulphate at hand, while it is easy to see that a coating of oxygen would lower the potential at first. The conclusion is, moreover, reinforced by the fact that the same potential is attained from the opposite direction by the gradual falling off of a higher potential artificially and temporarily created in the metallic electrode with the help of hydrogen conveyed to the system from without, as will be explained in the succeeding section of the paper. Hence there can be little doubt that the potential of porous iron reduced at about 1,000° and immersed in normal ferrous sulphate is really as high as $0.79 - 0.612 = 0.18$ volt, if the decinormal calomel electrode is taken as 0.612, the normal calomel electrode being taken as 0.56. Pure iron which has been fused in a vacuum gives a value nearly 0.03 volt lower, or about 0.15 volt. This latter value, corresponding to the flat surface of a coherent mass, is the one to be chosen ordinarily as the normal value. Even this is nearly twice as large as that usually ascribed to it. The errors of the work of others were probably insufficient time of immersion and the presence of acid in the electrolyte, both of these tending to lower the observed value, as is shown above.

PART II. THE ELECTROMOTIVE FORCE OF IRON CONTAINING OCCLUDED HYDROGEN.

The fact that hydrogen freely penetrates iron at red heat and that iron retains some of this hydrogen on cooling was discovered as long ago as 1866 by Graham; but the more detailed study of this and related phenomena has been undertaken only in recent years, after its importance in the metallurgy of the metal had been established. Many papers have been published on this topic, but the field has been by no means thoroughly treated.

Our attention during this research was first directed to the well-known affinity of iron for hydrogen by observing the copious evolution of this gas from metal reduced at a low temperature.[a] Iron obtained from the oxide at 570° is, as well known, a fine powder, which oxidizes easily, and hence after even a short exposure to the air gives a low electromotive force. In order to test properly the free energy of such iron, it must be cooled in pure hydrogen and tested instantly after opening the reduction-tube. In this way it was found that the potential is not essentially different from iron reduced at 700°, being about 0.795 volt in conjunction with the decinormal electrode.

Nevertheless, such powder, upon immersion in ferrous sulphate evolved copious bubbles of gas, which were proved to be hydrogen. That this hydrogen was not in any extraordinary condition is shown by the fact that it neither altered the potential of the iron nor caused the iron containing it to produce any unusual reducing effect on mildly oxidizing solutions. It is probable that the hydrogen thus held by the fine powder was merely adsorbed, as the gas is adsorbed by charcoal.

That the gas could exist in the metal in a radically different condition we did not at first suspect; but this conclusion was forced upon us by the surprising and quite unexpected results of several other experiments.

In the first place, several pieces of porous iron which had been reduced at high temperature, slightly oxidized by long standing in the air, and then reheated in hydrogen at 575° gave at first an extraordinarily high value for the usual cell couple, namely 0.825. In seven hours this had decreased to 0.810, and in five days became constant at 0.798, essentially the normal value.

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[a] Baxter has shown that pure iron reduced at a high temperature contains but little occluded hydrogen. Am. Chem. Journ., 22, 363 (1899).

A slight indication of an excessive value of this kind had already appeared in other previous samples, many of which after a short immersion in ferrous sulphate showed a slight maximum. This was noticeable even in samples which had been ignited in a vacuum. In the cases mentioned at the beginning of this paragraph, after standing some time, bubbles of hydrogen appeared around the metal, as the electromotive force decreased. This seemed to show that in some way the excessive electromotive force was connected with hydrogen. But hydrogen gas has a lower, not a higher potential than iron. Therefore, it is clear that if the abnormality is produced by hydrogen, this impurity must exist in the metal in a different form—no longer as merely adsorbed gas on the surface of the fine powder, but in some new state, inclosed in the less open structure of the sintered iron.

More light was thrown upon all these matters by interesting series of experiments which showed that the dissolved active hydrogen could be more easily introduced into the iron in other ways. There follows a brief description of these experiments.

The first series furnishing this further light was a set of experiments originally begun as a preliminary attempt to cause a change in the internal structure of iron by quick cooling. In it iron was plunged while hot into water.

In order to quench iron suddenly from a high temperature without coating the metal with a hardly soluble film of oxide, it was clearly necessary to conduct in an atmosphere free from oxygen both the heating of the metal and the transference to the cooling agent.

An atmosphere of hydrogen was first used for this purpose. As before, a stout tube of Berlin porcelain was erected in a vertical position, the middle portion being heated by a Fletcher furnace. Pure electrolytic hydrogen, thoroughly washed and dried, was supplied at the top of the tube through a cooled Hempel stopper, which was further protected against the rapid convection of hot hydrogen by a pipe-bowl suspended at the upper limit of the heated zone by means of an iron wire. The iron was heated at first in an unglazed basket of the best porcelain, and in the later experiments on a shelf or disk of the same material. Simple mechanical devices as before enabled the iron to be plunged or dropped quickly into the cooling agent at the base of the tube. The temperature of heating was determined by a Le Chatelier platinum-rhodium thermoelectric junction. Cold boiled water was used as the cooling agent at the base of the tube, the operation being, therefore, merely the quenching of pure iron without exposure to oxygen gas.

Even the first experiments gave interesting results. Porous iron reduced at 800° was quenched from 1,000°. Twenty minutes afterwards the superficially oxidized sample was immersed in ferrous sulphate and half an hour later it gave the value 0.89 volt against the decinormal electrode, instead of only 0.79 as before. This extraordinary value was only temporary, the electromotive force falling rapidly, at the end of one hour being 0.825 volt and of five hours, 0.803. Three other pieces quenched at the same time gave similar results. Because the electromotive force fell rapidly it appeared possible that an immediate reading might have given even higher results. A repetition of the experiment with frequent readings was evidently very desirable.

The second quenching was a repetition of the first. To remove the adhering water after the operation, the samples of iron were rinsed for a minute or two in ferrous sulphate solution before putting into the cells, thus preventing dilution of the normal solution in which they were measured. The results verified those of the first quenching, but added to them, in that the later ones showed the speed of decrease in potential to be much less in the first half hour than afterwards. The potential started at about 0.9 volt, and after remaining almost constant for thirty minutes began to fall off rapidly. A number of other similar quenchings were made, most of which gave similar results, only a few showing no excess of potential. Typical examples are given in the following table, under the heading, Sample 44.

Further experiments were made to determine if the temperature before quenching caused any considerable effect on the results.

The apparatus used was the same as the one which served in the previous experiments. One sample was quenched from 695° and another from 600°. In both cases the quenched iron rose to a maximum electromotive force less strikingly above the normal value, the former attaining 0.87 volt and the latter 0.82 volt, which potentials, as usual, settled down to the normal values of 0.795 in the course of half a day. These experiments showed that the excessive value of the electromotive force was directly dependent upon the temperature before quenching, a higher temperature giving a greater excess. They added to the evidence already given that the "gamma" or high-temperature phase of iron could have nothing to do with the excessive values, because the latest quenching occurred from a temperature below the recognized transition point. It will be remembered in this connection that pure iron quenched from 1,100° on a cold iron plate gave normal values for its electromotive force.

The experiment was next made of reheating the quenched iron in hydrogen in order to discover whether or not it would return to its normal condition. Two pieces of this same quenched iron were thoroughly dried in alcohol and ether and three days later were reheated in hydrogen for one hour (the highest temperature being faint redness) and then slowly cooled.

The results, together with those of the previously described quenched iron, are given in the following table:

TABLE 8.—*The effect of reheating quenched iron.*

Time elapsed after immersion.	Sample 44, quenched, not reheated.		Sample 45, reheated iron.	Sample 46, reheated iron.
	Fresh.	Exposed to air.		
	Volt.	Volt.	Volt.	Volt.
0^h 3^m	0.880	0.79	0.796	0.794
0 11	0.910	0.80	0.800	0.801
0 20	0.906	0.90	0.800	0.804
0 45	0.890	0.89	0.797	0.804
2	0.810	0.81	0.797	0.808
4	0.797	0.80	0.797	0.802

It is clear at once that samples 45 and 46 had once more acquired the same condition they possessed before they were quenched—as was to be expected. Thus there can be no doubt that the reheated iron returns essentially to its normal condition.

From these experiments it was clear that something, either chemical or physical, had happened to the iron during its heating and plunge into water which caused it to assume an excessive potential. Two possible causes might underlie these interesting results. Either the sudden cooling might have preserved the iron in an unstable allotropic form yielding a higher electromotive force, or else occluded hydrogen might in some way be responsible for the differences. The former of these explanations was disproved by the already described experiments on cooling iron in a vacuum on a cold iron plate. Hence only the latter explanation remained, and the phenomenon was obviously to be classed with the occlusion of hydrogen from the hot gas.

It now became an interesting matter to find whether this hydrogen came from the hydrogen gas or from the water during the instant of quenching. This was easily decided by an experiment in which the metal was heated in and quenched from an atmosphere of *nitrogen*. The quenching apparatus was exactly the same as that used in all the previous experiments. The nitrogen was prepared by Wanklyn's method of blowing air through aqua ammonia, passing this ammoniacal air over hot copper gauze, and purifying the resulting nitrogen in the usual way. All rubber used in the apparatus had been boiled in caustic solution and was thickly coated on the inside with the semi-solid paraffin. In this apparatus a typical sample of porous iron was heated for twelve minutes in nitrogen at a temperature of 1,040° and was then quenched in ice-water. Of the two pieces thus quenched, one was immersed in the ferrous sulphate solution five minutes after quenching, while the other was thoroughly dried in alcohol and ether and put into the cell to be measured on the following day.

The results agreed in a general way with those already obtained by quenching from an atmosphere of hydrogen. They differed in two respects. The maximum electromotive force was 0.03 volt higher than any other thus far obtained, rising to 0.94 volt, and this high electromotive force was retained for a much longer period of time. These are differences in degree only, and since the other results differed among themselves, although to a less extent, the higher value is to be ascribed merely to more favorable experimental conditions.

Could the formation of iron nitride in any way have produced the high potential in this case? Reflection promptly decided this question in the negative. Iron nitride is formed only at low temperatures and is decomposed even in a stream of ammonia at higher temperatures; " free nitrogen is not able to unite with iron, even when the latter is reduced in nitrogen, and the formation of nitride is dependent on the coming in contact of nascent nitrogen with iron."[33] Moreover, the nitride begins to decompose in a stream of nitrogen at 600°, and the nitride Fe_2N is an exothermic compound. Hence probably it has a lower electromotive force than iron,[34] not a higher one, and the nitride is evidently out of the question.

Upon standing in ferrous solution the quenched iron evolved an appreciable volume of gas, which was shown to be hydrogen by explosion with oxygen in a micro-eudiometer.

In view of this fact, and because iron quenched from nitrogen gave the same high potential as iron quenched from hydrogen, there can be no doubt that the bulk of the occluded hydrogen must have come from the water at the moment of quenching. Some of the iron must have been oxidized, and the resulting nascent hydrogen must have dissolved in the iron, in its active state. No other explanation seemed to be compatible with the extraordinary potential observed.

Other workers on this subject (for example Heyn,[35] who found that hydrogen exists in iron quenched from above 730° in an atmosphere of hydrogen) have usually supposed that the occluded impurity was taken from the gas and not from the water, but our experiments show conclusively that the water is the source of the greater part of the hydrogen.

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[33] Stahlschmidt, Pogg. Ann., 125, 37 (1865).

[34] Assuming total energy change to be an approximate guide to free energy change in reactions of this kind.

[35] Stahl und Eisen, 20, 837 (1900). See also Roberts-Austen, Fifth report of the Alloys Research Committee, Proc. Inst. Mech. Eng., 1899, p. 35.

The discovery that in this case nascent hydrogen may be absorbed more freely than the gaseous material by iron at once reminded us of the well-known absorption of the light element by metals used as a cathode in acid solutions. Cailletet[illegible] and Johnson[illegible] showed in 1875 that iron will take up at ordinary temperatures electrolytic hydrogen deposited upon it, while ordinary gaseous hydrogen has no effect. Johnson's work was particularly interesting. His iron was in the form of soft wire and his simple method of testing for hydrogen was to bend the wire to test its brittleness, since he had discovered the interesting fact that hydrogen imparted this property to iron previously tough. Immersing the wire in acids which react on it to form hydrogen uniformly made it brittle. Also when the fractured surface was wetted with water it was seen to froth. Making the wire the cathode in neutral, acid, or alkaline solutions had the same effect, but iron anodes were unaffected even in the acid solution. Other wires were placed in a bottle full of water and hydrogen was made to bubble violently through the water, without any trace of absorption.

Another interesting research yielding similar results was conducted by Bellati and Lussana.[illegible] A barometer was closed at the top by an iron plate, and by cementing a glass ring on this an electrolytic cell was made in which hydrogen was generated at the iron plate; the mercury at once fell by diffusion of the hydrogen through the plate into the barometric vacuum. This work was later confirmed and amplified by Shields.[illegible]

In view of these phenomena, it became a very interesting point to discover if the active hydrogen introduced into cathode iron from solution is capable of raising the potential of a normal cell to the value of 0.93, that observed with spongy iron quenched from 1,100° in nitrogen. Shields had already observed that this occluded hydrogen raised the electromotive force of the iron above the normal value, but the maximum had not been determined.

This point was easily tested. In order to obtain satisfactory evidence it is of course necessary that iron alone should be immersed as cathode; the platinum wire supporting it must be above the liquid. Preliminary experiments showed that a large excess of potential is as a matter of fact attained, but that it falls off with very great rapidity. Spongy iron which had been

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[illegible] Comptes rendus, **80**, 319 (1875).

[illegible] Proc. Roy Soc. (London), **23**, 168 (1875).

[illegible] Bellati and Lussana, Z. Phys. Chem., **7**, 229 (1891).

[illegible] Shields, Chem. News, **65**, 195 (1892). Further discussion of this matter will be found in papers mentioned later; see also Hoitsema, Z. Phys. Chem., **17**, 1 (1895); Winkelmann, Drude's Ann., **8**, 388 (1902); Richardson, Nicholl and Parnell, Phil. Mag. (6), **8**, 1 (1904). St. Schmidt considers the assumption of a split of the hydrogen molecule to be unnecessary and unwarranted. (Drude's Ann., **13**, 747 (1904).)

made the cathode of a dense current in an acid solution for an hour was quickly washed with neutral ferrous sulphate, and was measured as soon as possible. In half a minute after immersion it had sunk to 0.822 volt, in four minutes later 0.800, and in an hour to constancy at 0.790. Evidently the hydrogen is only very superficially deposited, and most of it is gone before measurement is possible. Longer exposure as cathode might have more effect. Much more striking results were obtained from electrolytic iron obtained from a neutral solution with the help of a current so dense as to deposit hydrogen with the iron. Such a specimen (sample 48), measured about three seconds after the breaking of the current, gave a potential of 0.93, equal to that observed in the quenched iron. In a minute this had sunk to 0.85 volt; but even after an hour it remained as high as 0.83 volt, not sinking to about the normal value 0.798 for several days.

Thus it is clear that as far as potential measurements can show, the hydrogen driven into iron with the help of electrical energy is essentially similar to that absorbed in the act of quenching, although the latter operation seems to be especially favorable to the occlusion. Probably the action of the red-hot core upon the steam produced by the exterior of the porous metal supplies the nascent hydrogen to the iron at a temperature especially suitable for occlusion.

It is interesting to note that even without outside electrical assistance hydrogen in this active form may be taken up by iron from acid solutions. Upon immersing the metal in an acid solution of ferrous sulphate, hydrogen is of course evolved, and the potential of the iron while still in the acid is lowered as much as two decivolts—evidently by the coating of gas, for hydrogen gas has a potential much lower than iron. But besides this superficial effect, a more deep-seated one is occurring, as is easily shown.

Upon removing this iron quickly to a neutral solution of ferrous sulphate and measuring at once, its potential is found to be above the normal value, the usual cell often reading as high as 0.83 instead of 0.78 or 0.79. In a few hours it settles down as usual to its normal level, evolving in the process bubbles of hydrogen gas. The iron alone could not of course raise the active hydrogen which it absorbs to a concentration above that capable of giving an electromotive force equal to its own (0.79 with the decinormal electrode), but with the help of the osmotic pressure of the ionized hydrogen in the acid more hydrogen is driven in. This excess manifests its potential and changes to hydrogen gas when the surrounding acid is removed. As a change of only tenfold in the concentration of the ionized hydrogen would be expected to produce a change of potential of nearly 0.06 volt, the observed effect is by no means excessively large. Stated in another way, it may be said that the hydrogen taken in by iron from an acid solution is in equilibrium with *nascent* hydrogen, and therefore possesses a high chemical potential.

In the course of the quenching experiments it was found that iron charged with active hydrogen lost its impurity much more quickly when immersed in ferrous sulphate than when immersed in water or kept in air. This interesting fact seemed worthy of more careful study, because it might be capable of throwing light on the singular occlusion. Accordingly the following series of experiments was instituted upon six pieces of iron, all quenched at once under such conditions that all were exactly alike:

Piece No. 51 was immersed in ferrous sulphate and measured immediately after quenching. Its electromotive force began at about 0.8 volt, gave the maximum value 0.91 volt after a few minutes, and then fell off as before, reaching 0.90 volt in half an hour and 0.793 volt in four hours.

No. 52 was left in the water in which it was quenched for an hour and twenty minutes before measurement. When the electromotive force had reached its maximum of 0.90 volt after 26 minutes subsequent immersion in ferrous sulphate, No. 51 had passed that point over an hour and a half before.

No. 53 was also left in water and was first measured after two hours and forty minutes had elapsed. By the time it gave its highest electromotive force, 0.91 volt, No. 1 had dropped to 0.803 volt.

No. 54 was left in water for 26 hours and then immersed in ferrous sulphate. It behaved but little differently from No. 53, but its maximum was lower, being only 0.85 volt. Before its immersion all the preceding had reached their constant values 0.795.

No. 55 was thoroughly dried in alcohol and ether immediately after quenching and kept in a desiccator an equal length of time (26 hours) before measurement. This specimen began at 0.79 volt, rose regularly to 0.88 volt in two hours, and reached 0.80 volt again in twenty-four hours.

No. 56 also was immediately thoroughly dried and was measured after 73 hours, giving a similar but less marked maximum (0.85 volt).

The whole series of experiments was then repeated with essentially identical results.

The comparison of the results of these series of experiments shows that mere exposure to dry air slowly lowers the high electromotive force due to quenching, that pure water hastens this lowering a very little more than exposure to the air, but that immersion in ferrous sulphate quickly establishes equilibrium. The more typical of these experiments, with some of the previous ones, are plotted in figure 6.

It became now an interesting matter to discover if any other electrolyte would effect the adjustment of equilibrium as quickly as the ferrous sulphate. In an easily carried out variation on the preceding series, a normal solution of potassic suphate was used as a typical electrolyte. Brief immersion in this solution seemed to show no more effect in discharging the hydrogen than in water, but long immersion showed a slight difference in favor of the electrolyte. The rate was nevertheless so much slower than that observed in the case of ferrous sulphate as to indicate entirely another mechanism of reaction.

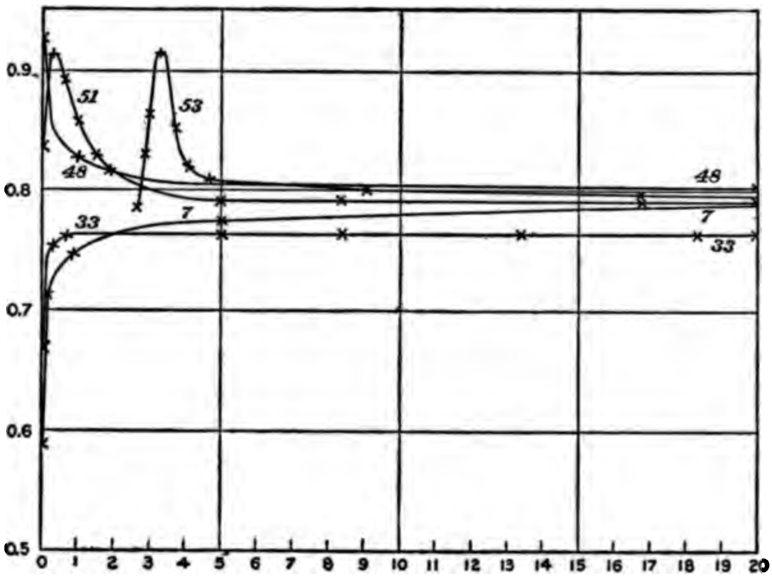

FIG. 6.—THE CHANGING POTENTIAL OF THE IRON ELECTRODE.

In the direction of ordinates are plotted the potentials of the iron electrodes in normal sulphate, in combination with a decinormal calomel electrode. Time in hours is plotted in the direction of abscissæ. The curves are typical, No. 7 of porous iron which has been exposed to air, No. 33 of pure fused iron, No. 48 of porous iron which has been made a cathode, No. 51 of porous iron quenched in water, and No. 53 of the same after exposure to air for 2⅝ hours.

The progress of the evolution of the gas in ferrous sulphate may be supposed to be as follows: The active hydrogen, having a higher potential than the iron, causes metal to deposit from the ferrous sulphate, and the acid thus formed immediately attacks the deposit, or a neighboring portion of metal. Without the interposition of the iron as carrier, the hydrogen seems to find it difficult to go from its occluded to its gaseous state. When an electrolyte which contains no easily deionized cation is substituted for the ferrous sulphate, the reaction involving deposition can not take place, and the hydrogen remains in its occluded condition.

These considerations show further that the final potential which the iron attains after long immersion in ferrous sulphate is probably the true potential, because, since both iron and ferrous sulphate are greatly in excess, the equilibrium finally attained must correspond to these two alone. Even if some dissolved hydrogen is retained by the iron it can not possess a permanent potential above that of the iron. That this is true is shown by the fact that quenched iron finally attains a potential equal to that finally attained by a similar sample which has been long exposed to the air—one approaching this value from above, the other from below.

The attempt to explain the nature and condition of the active hydrogen in iron is assisted by a suggestive paragraph which occurs in a paper by Thos. Graham[40] "On the relation of hydrogen to palladium and on hydrogenium":

> The chemical properties of hydrogenium[41] also distinguish it from ordinary hydrogen. The palladium alloy precipitates mercury and calomel from a solution of the chloride of mercury without any disengagement of hydrogen; that is, hydrogenium decomposes chloride of mercury, while hydrogen does not. . . . Hydrogenium (associated with palladium) unites with chlorine and iodine in the dark, converts red prussiate of potash into yellow prussiate, and has considerable deoxidizing powers. It appears to be the active form of hydrogen as ozone is of oxygen.

Of these chemical tests one was easily extended to hydrogen contained in iron. It was found that carefully cleaned pure iron wire, and also porous iron which had been kept for a year in the pure air of a desiccator over potash, had no appreciable tendency to reduce neutral potassic ferricyanide. Even after the iron had stood in a solution of this salt for five days the solution gave no precipitate with ferric chloride. Such iron was evidently practically free from active hydrogen. On the other hand, iron which had been freshly made showed a marked reducing tendency, and this tendency was even greater in quenched iron and iron which had been used as a cathode (or had been simply immersed in acid) and thoroughly washed. These results are quite in accord with the potential measurements already recorded, and furnish additional evidences of active hydrogen in freshly reduced or quenched iron, but point to its absence on the surface of iron long exposed to the air.

In what form may this hydrogen be supposed to exist? Ramsay was perhaps the first to suggest that hydrogen undergoes dissociation when passing through a hot metal, or through one made a cathode in acid solution.[42] Our experience supports this hypothesis, and seems to be explicable in no other way. In one respect only does Ramsay's opinion appear questionable, namely, in his assumption that the dissociated gas is ionized.[43] In recent years the word ion has been used in so many senses that an unfortunate vagueness has crept into its definition; but the idea of ionization seems always at least to be associated with electric charges. Now, in this case there seems to be no need of assumption of an electric charge on the occluded hydrogen atom; indeed it is hard to see how much a charge could be held in the midst of so good a conductor as iron. To the writers it appears much more probable that the hydrogen is rather in the condition of nascent hydrogen, set free from the positive charges which had caused it to ionize in the aqueous solution, but not yet consolidated into the form of hydrogen gas. It would appear that iron is permeated with minute cavities into which only this dissociated form of hydrogen is able to enter, and that upon all occasions when the nascent element is liberated in the presence of the iron, the opportunity of entrance is at once seized. In the wording of the atomic hypothesis, the active hydrogen occluded by iron seems to be atomic but not ionized hydrogen, very different in its properties from the molecular hydrogen which is adsorbed by the fine powder reduuced at low temperatures.

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[40] Proc. Roy. Soc. (London), **17**, 219 (1869); Collected Papers, p. 290-299; Pogg. Ann., **138**, 49 (1869).

[41] Hydrogenium = hydrogen in a metal.

[42] Sir William Ramsay, Phil. Mag., 5, **38**, 206 (1894).

In conclusion, it is a pleasure to express our gratitude to the Carnegie Institution of Washington for generous pecuniary assistance in this investigation.

SUMMARY OF PART FIRST.

(1) A method, both rapid and convenient, is given for the preparation of iron containing no impurity but hydrogen.

(2) The potential of this spongy iron in ferrous sulphate was measured and found to be at first greatly affected by previous exposure to the air. After long immersion in ferrous sulphate solution a constant and trustworthy value was reached.

(3) Even the enormous pressure of about 350,000 kilograms per square centimeter did not produce any appreciable permanent change in this value, although the masses were effectively cold-welded. Taken in conjunction with the results of Spring, this fact is shown to be consistent with the hypothesis of compressible atoms.

(4) Measurements of the free-energy change in iron during a pull upon a wire great enough to cause rupture gave results showing that this change must be very small, and called attention to regrettable errors in previous work on this subject.

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[43] Ramsay, "Modern Chemistry," II, 31 (London, Dent, 1904).

(5) Iron reduced at a low temperature was found to have an electromotive force higher by at least 0.02 volt than iron which had been fused. If the normal calomel electrode is taken as having a single potential difference of 0.56, pure compact iron has a single potential difference of 0.15, and spongy or porous iron about 0.17 to 0.18 volt. The former is to be chosen as the normal value. It is pointed out that the much lower results of others are probably to be referred to the acidity of their solutions and to insufficient waiting for equilibrium.

(6) No important change in these values was caused by sudden cooling from a high temperature.

(7) Speculations concerning the relations of these facts to the structure and internal pressure and solubility of iron are tentatively recorded. The difference of potential of the different forms of iron is probably but not certainly to be referred to the different sizes of their separate particles.

SUMMARY OF PART SECOND.

(8) It was found that hydrogen could be taken up by finely powdered iron reduced at low temperatures without affecting the metal's electromotive force. When the metal is wholly coated with hydrogen the electromotive force is diminished. It is probable that hydrogen thus held is merely adsorbed or held as molecular hydrogen.

(9) It was found further that by quenching in water, whether from hydrogen or from nitrogen gas, that iron takes up hydrogen in an active form, raising the single potential by as much as 0.15 volt. This hydrogen is quickly expelled in ferrous sulphate solution, and very slowly in water or potassic sulphate solution, the potential returning to the normal value. The gas thus evolved was proved to be hydrogen gas.

(10) A small amount of hydrogen in the same active form may be taken in from hot hydrogen gas.

(11) Active hydrogen thus occluded by iron seems to be in every way similar to that occluded by iron in the presence of nascent hydrogen, whether this is chemically or electrolytically produced.

(12) It is pointed out that the most reasonable explanation of these facts is to suppose that the active dissolved hydrogen is dissociated but not ionized.

The investigation will be continued in the near future.

CONDENSATION OF VAPOR AS INDUCED BY NUCLEI AND IONS

By CARL BARUS

Hazard Professor of Physics, Brown University

1902

WASHINGTON, D. C.:
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PREFACE.

The chief purpose of the present volume is the development of a fog chamber of simplest practical character, capacious enough to admit of the measurement of the largest available coronas, and efficient up to the highest exhaustions applicable; *i. e.*, those which do not uselessly overstep the optical limits of the experiment, where fog particles become so fine as to be virtually inactive in diffracting or scattering white light. This I think has been accomplished, and the results, as far as they go, seem to indicate an efficiency not inferior to Wilson's piston apparatus. I have not, however, been able to get much beyond the large green-blue-purple corona, no matter whether the nuclei selected were effectively large, like the ions, or effectively small, like the colloidal nuclei. The forms beyond are flimsy and so nearly colorless as to be useless for measurement; but the steam-jet nevertheless reveals a whole order of axial oranges and yellows, lying beyond, which to my knowledge have not been detected in any form of fog chamber whatever.

As used in most experiments, including my own earlier work, the fog chamber with a plug stopcock seems to be of very inferior efficiency in comparison with the piston form. This, however, in a properly designed apparatus, is the case only when the attempt is made to obtain the isothermal drop in pressure observationally at the fog chamber, closed at once after exhaustion. The datum needed can only be found by computation, and the initial pressures in the fog and vacuum chambers and their final pressure when in contact, always at the same temperature, suffice for this purpose. Though I was prepared for some corrections, I did not anticipate so large a difference between the apparent drop and the true drop of pressure, as actually appears. In the experiments which follow, the ratio is in fact as 1,000 to 775, a difference of nearly 25 per cent. Hence it will be necessary to restandardize the coronas with this result in view, an undertaking which I hope to begin in the near future. Indeed a large number of incidental results would have made this desirable in the interest of other investigations. For similar reasons I have (as a rule) continued to refer the nucleations of the present volume to the drop in pressure *observed* at the fog chamber; and such reference is sufficient for the comparisons aimed at, if the same type of apparatus is used throughout, as was the case.

Having improved the fog chamber to the degree shown in Chapters I and II, it was made use of in Chapter III for certain incidental experiments. I have already shown in case of dust-free air and the persistent nuclei produced by intense X-radiation that the distribution of nuclei within the fog chamber is a most remarkable feature of the experiment. The same, however, is true of the ions. Whether produced by X-rays acting from long distances or by radium, the density of ionization is as a rule very different in different parts of the fog chamber, showing the important effects due to the presence of secondary radiation within. Again, the change of nucleation produced when the exciting cause (X-ray bulb or radium tube) is removed at different distances from the fog chamber was to be reinvestigated. Associated with this experiment is the occurrence of minima of nucleation for certain distances, supposing the exhaustion to be sufficiently high to induce condensation of ions and colloidal nuclei in presence of each other. Finally, if the rate of decay of ions can be inferred from independent electrical experiments, a method for the standardization of coronas is presented which bids fair to be the most satisfactory solution of the problem suggested. The method admits of a determination not only of the relation of the nuclei corresponding, in a given case, to two different coronas (*cæt. par.*), but of the absolute nucleation involved. There is also a possibility of detecting in this way how a given mass of precipitated water is distributed among nuclei of different sizes when occurring together—one of the most important of the problems outstanding in connection with this apparatus.

Chapter IV adduces a variety of results for colloidal nuclei in media other than air-water. It is shown, for instance, that there is no evidence to prove the colloidal nuclei in a medium of carbon dioxide and water are larger than in the normal case of air and water, in spite of the presence of the coercible gas in which groups of larger molecular aggregates would be anticipated. On the other hand relatively large colloidal nuclei do seem to occur in a medium of air and alcohol vapor. Thus it is suggested that colloidal nuclei in dust-free wet air are to be associated with the saturated vapor and that the gas is only secondarily involved.

In Chapter V, undertaken by Miss L. B. Joslin under my direction, a systematic comparison is worked out of the relations between the number of ions in the atmosphere and the corresponding dust contents in the lapse of time. No direct connection is apparent, whence it follows that as the nucleation is largely of local origin, other sources must be looked to for the ionization, or that the enormous local output of ions from an industrial community vanishes so rapidly as to be quite negligible. On the other hand, it may be possible to detect evidences of "absorption" in the curves obtained. Incidentally the nucleation of the atmosphere of Providence during nearly four years is exhibited.

Finally, in Chapter VI, I return to the problem begun in Chapter I, to see whether there is any change in the colloidal nucleation of dust-free air, such as might be ascribed to the ionization produced by some penetrating cosmical radiations coming from without; for it was to be the plan of these researches to study the ordinary dust content of the atmosphere with regard to its variation in the lapse of time first, and thereafter to continue in the same way with the nucleation of the dust-free atmosphere. This nucleation is found to *increase* synchronously with the *decrement* of the barometer; but as the amount of adiabatic cooling, *i. e.*, the efficiency of the apparatus (*cæt. par.*), follows the same conditions, it is extremely difficult to disentangle the two effects. Nevertheless the results are of considerable interest and they are therefore reported in their present state of progress.

My thanks are due to Miss L. B. Joslin, who not only gave efficient assistance in the preparation of the manuscript and of the drawings for the press, but contributed much of the work in Chapter III, section 62, and Chapter V.

CARL BARUS.

CONTENTS.

CHAPTER I.—*Early Successive Stages of Efficiency of the Fog Chamber and Allied Results.*

DISTRIBUTION OF NUCLEI WITHIN THE FOG CHAMBER ENERGIZED BY THE GAMMA-RAYS OF RADIUM, AND BY THE X-RAYS.

		Page.
1.	Introductory	1
2.	Data	3
3.	Explanation	5
4.	Further experiments with radium. High exhaustions	5
5.	The same, continued. X-rays	6
6.	The same, continued. Miscellaneous tests	7
7.	Distance effects of radium	9
8.	Cause of the minimum and the maximum	10
9.	Further experiments with radium	12
10.	Distance effect of penetrating X-radiation	12
11.	General inferences (radiant fields)	13

THE NUCLEATION OF FILTERED AIR IN RELATION TO DIFFERENT SUPERSATURATIONS OF WATER VAPOR.

12.	Successive series of results	13
13.	Effect of X-rays and gamma-rays. Data	18
14.	Persistent nuclei	18
15.	Persistent nuclei generated through tin plate	20
16.	Discussion	21
17.	More rapid exhaustion. Apparatus and data	23
18.	Remarks on the s-curves. Non-energized air	25
19.	The same, continued	26
20.	The same, continued. Action of radium	27
21.	The same, continued. Action of X-rays	27
22.	Remarks on the n-curves. Non-energized air	27
23.	The same. Action of radium	29
24.	The same. Action of X-rays	29
25.	Remarks on the N-curves	29

THE NUCLEATION OF FILTERED AIR IN THE LAPSE OF TIME.

26.	Method	30
27.	Early data	30
28.	Apparatus modified	31
29.	Inferences	31

SUMMARY OF THE RESULTS OF THE CHAPTER.

30.	Distribution of ions within the fog chamber	32
31.	Minimum of efficient nucleation	32
32.	Persistent nuclei	32
33.	Dependence of efficiency of fog chamber on the size of the exhaust pipes	33
34.	Invariable character of colloidal nucleation in the lapse of time	33

CHAPTER II.—*Later and Final Stages in the Efficiency of the Fog Chamber due to a Gradual Increase in the Bore of the Exhaust Pipes.*

CONNECTING PIPES NOT LARGER THAN 1.5 INCHES IN DIAMETER.

Page.
35. Introductory 34
36. Examples of data for 1-inch connecting pipes 35
37. Data for pipes 1½ inches in diameter 35
38. The same, continued. Shorter pipes 38

CONNECTING PIPES 2 INCHES IN DIAMETER.

39. Remarks on the method 41
40. Data for pipes 2 inches in diameter, 12 inches long 42
41. The same, continued. X-ray bulb inclosed in lead 44
42. Discussion 45
43. Radiant fields 49

COLLOIDAL NUCLEI IN DUST-FREE AIR. EXHAUSTION PIPES AND STOPCOCKS 4 INCHES IN DIAMETER.

44. Purpose 51
45. Apparatus 51
46. Exhaustion difficulties 53
47. Same, continued. Case of air in fog chamber saturated with water vapor ... 55
48. Case of saturated air in both chambers 59
49. Observations with 4-inch exhaust pipes 65
50. Observations, continued 70
51. The same, continued 71
52. Discussion 73
53. Summary 73

CHAPTER III.—*Miscellaneous Experiments.*

54. Objects 77
55. Growth of persistent nuclei 77
56. Water nuclei produced by evaporation 78
57. Distance effects. X-rays 82
58. The same, continued. Small wood fog chamber 85
59. The same, continued. Large wood fog chamber 85
60. The same, continued. Discussion 86
61. Distance effect and absorption. Radium 89
62. Falling to pieces of ions in the lapse of time 91
63. Decay curve 95
64. The same, continued 97
65. Condensation phenomena of the inclosed steam jet. Methods and results ... 98
66. Summary 102

CHAPTER IV.—*Distribution of Colloidal Nuclei and of Ions in Media other than Air-water.*

COLLOIDAL NUCLEI AND IONS IN WET DUST-FREE CARBON DIOXIDE AND IN WET COAL-GAS.

67. Apparatus 105
68. Data for carbon dioxide 105
69. Behavior of carbon dioxide 107
70. Cause of differences 107

Page.
71. Nucleation increases subject to a uniform law of equilibrium ... 109
72. Data for coal gas ... 110
73. Character of the early results for coal gas ... 110
74. New data for coal gas ... 111
75. Conclusion ... 112

COLLOIDAL NUCLEI AND IONS IN DUST-FREE AIR SATURATED WITH ALCOHOL VAPOR.

76. Introductory ... 112
77. Apparatus and method ... 113
78. Properties of alcohol fog ... 113
79. Number of particles ... 113
80. Size of the nuclei ... 115
81. Data for alcohol vapor ... 118

ABSENCE OF COLLOIDAL NUCLEI IN STRONG ODORS.

82. Introductory ... 120
83. Data for camphor, turpentine, naphthalene ... 120
84. Summary ... 121

CHAPTER V.—*The Cotemporaneous Variations of the Nucleation and the Ionisation of the Atmosphere of Providence. By Lulu B. Joslin.*

85. Introduction ... 123
86. Measurements of nucleation ... 124
87. Data for nucleation ... 125
88. Remarks on the table of nucleation ... 125
89. Mean daily nucleation ... 125
90. Mean monthly nucleations ... 141
91. Measurement of ionization ... 141
92. Data for ionization ... 143
93. Remarks on the tables ... 149
94. Errors of measurement ... 150
95. Mean daily ionization ... 152
96. Mean monthly ionizations and conclusion ... 153

CHAPTER VI.—*The Variations of the Colloidal Nucleation of Dust-Free Air in the Lapse of Time.*

97. Introductory ... 155
98. Method and data ... 155
99. Deductions ... 157
100. Effect of the barometer ... 158
101. Corrections ... 159
102. Further data ... 160
103. Conclusion ... 164

CHAPTER I

EARLY SUCCESSIVE STAGES OF THE EFFICIENCY OF THE FOG CHAMBER AND ALLIED RESULTS.

Before beginning the main subject of this chapter (see section 2), it is advisable to add a few measurements of the distributions of ions produced within the fog chamber by the X-rays or by radium acting from without, since these occurrences must be kept in mind throughout the measurements. Again, the effect of different classes of nuclei (persistent nuclei, ions, and colloidal nuclei) in presence of each other is similarly important and direct light must be thrown upon it preliminarily.

Under all conditions the fog chamber is attached to a large vacuum chamber by a rigid passage-way of the length and diameter specified, the ratio of the volumes of the two chambers being about as 6 to 100, respectively. Moreover, it was customary to read off the drop of pressure (δp) at the fog chamber (isolated immediately after exhaustion from the vacuum chamber) when isothermal conditions had been reestablished. The observed datum suffices for the comparisons of nucleation when the same chambers are used throughout; but it will be shown in Chapter II that it is much in excess of the true drop of pressure and that the latter is to be computed from the initial pressures in fog and vacuum chambers and the final pressure when both are in contact, all under isothermal conditions.

After completing the work of section 2 of this chapter, a few applications were made with the apparatus in its state of partial completion for the purpose of ascertaining whether there is any discernible change of colloidal nucleation and by implication of ionization in the stagnant air within the scope of the method. Several months of observation showed none. The early data have been added to the chapter for convenience in chronology, though they slightly interrupt the continuity of the research. The question of time variation is taken up again by a different method in Chapter VI.

DISTRIBUTION OF NUCLEI WITHIN THE GLASS FOG CHAMBER, WHEN THE AIR IS ENERGIZED BY THE GAMMA-RAYS OR THE X-RAYS.

1. Introductory.—I may recall at the outset that there are three classes of nuclei to be considered in this chapter, the first of which includes the ordinary dust-like or persistent kind. They may be separated from the air by the filter and they require the smallest degree of supersaturation of water vapor to precipitate condensation. They are usually but not always (necessarily) foreign bodies in the air; at least they are producible in dust-free air by the X-rays of sufficient intensity and by other radiation. The second class comprises the fleeting nuclei. They are often charged and then called ions. They persist for very short periods of time, usually vanishing within a minute. They can be maintained, therefore, only in the presence of radiation, corpuscular or undulatory, from which their intimate association with electrification or with ultra-violet light is manifest. Such radiation may occur spontaneously within the body of a gas during the state of generation. The sizes of these nuclei are intermediate between the first or dust-like class and the third class. This comprises the colloidal nuclei of dust-free air, which are *virtually* persistent, inasmuch as they are a structural part of the body of the gas and are reproduced as soon as removed. They require the highest degrees of supersaturation for condensation and are without electrification.

All these groups may be made to pass continuously into each other.

I shall use the term "nucleation" to denote the number of nuclei per cubic centimeter observed in any experiment. It will be understood that this means the *efficient* nucleation; for nuclei may be and usually are present, which are not detected by the exhaustion. They are computed in the present chapter from the angular diameter ($\phi = s/30$, nearly) of the coronas, for a given supersaturation. To specify their number one must come to a conclusion as to whether nuclei are removed more rapidly by the exhaustion than they can be replaced by the molecular system, or whether the reverse is the case. If fleeting nuclei and colloidal nuclei are supposed to be instantly reproduced we shall call the number n. None are then virtually removable by the sudden exhaustion. Otherwise the nucleation (corrected for the volume expansion) is called N. In this case the exhaustion is more rapid than the reproduction of nuclei. Both n and N, as well as s, will usually be given in the earlier tables; for the discrimination between n and N is not possible, and s is specially favorable to the small nucleation which are apt to be crowded out of the diagrams for n and N.

Returning to the subject of this section, I may state that the radium used was a weak sample (10 mg., 10,000×) hermetically sealed in a thin aluminum tube. In an earlier paper I showed that whereas the nucleation produced decreased very rapidly with the distance of the energizer from the outside of the cylindrical glass fog chamber, the number of nuclei within was apparently the same throughout the length of the axis. Pressure differences, however, were usually kept below the fog limit of air. As the aluminum tube was carefully sealed (ground screw plug and wax) the beta- and gamma-rays are here alone in question, and as the bottom of the fog chamber through which the radiation passes may be 1 cm. thick and the walls are everywhere more than 0.2 cm. thick, only the more penetrating beta-rays are active to reenforce the gamma-rays. In fact the earlier work showed that the rays after passing 1 cm. of lead produced an amount of nucleation only 30 per cent less than in the absence of the dense barrier. Thus the whole phenomenon is practically a question of the intensity of the gamma-rays.

In the course of the work, curiously enough a number of contradictory conclusions were reached, and it will therefore be advisable to report the results chronologically, beginning with the data for low pressure differences.

TABLE 1.—Distribution of nucleation within the glass fog chamber (43 cm. long, 14 cm. in diameter); nucleator, radium in thin aluminum tube. $\delta p = 21$ cm. Radium at D cm. from end, axially without. Lines of sight (two goniometers, s_1 and s_2) 15 cm. and 35 cm. from end nearest radium, or 20 cm. apart.

D	s_1	s_2	$N_1 \times 10^{-3}$	$10^{-3} \times N_2$	Mean $\left\{\begin{matrix} N_1 \\ N_2 \end{matrix}\right.$	Per cent.
0 cm.	3.5	3.3	19	16	17,200	...
	3.2	3.0	14	11	16,200	100
	3.4	3.4	17	17	......	...
	3.4	3.6	17	21	......	...
	3.5	3.3	19	16	......	...
20 cm.	2.5	2.5	7	7	7,000	45
	2.4	2.5	6	7	8,000	...
	2.6	2.8	8	9	......	...
40 cm.	1.8	2.0	3	3	4,000	24
	2.3	2.3	5	5	4,000	...
	2.3	2.3	4	4	......	...
∞ (air)	.0	.0	0	0	......	...

2. Data.—The cylindrical glass fog chamber (fig. 1), rigorously free from leakage, was placed, with its axis horizontal, in such a way that a prolongation of the latter intersected the radium tube at a distance, D. Two goniometers with their lines of sight about 20 cm. apart, and 15 and 35 cm. from the end (bottom) of the fog chamber nearest the radium tube, were used nearly at the same time for the measurement of the apertures of the coronas seen along the axis. Both were placed with the pins nearly contiguous to the walls of the cylinder, so that the eye was at a minimum distance of 30 cm. off. All the phenomena may in this case be more clearly observed and the small coronas are less liable to drop out before the measurement has been completed. The source of light

(Welsbach mantle) was 250 cm. beyond the fog chamber. Usually the angular diameter of the coronas is about $s/30$. In table 1, s_1 refers to the goniometer nearer the radium, s_2 to the other, and N_1 and N_2 are the corresponding nucleations, when D is the distance of the radium tube from the end of the cylinder.

After the influx of filtered air, time was always allowed for the dissipation of convection currents. There was some difficulty in reading both goniometers consecutively without loss of time, as the small coronas soon vanish with the subsidence of the fog particles. It was necessary to cleanse the walls carefully before beginning the work to obviate deposits of dew.

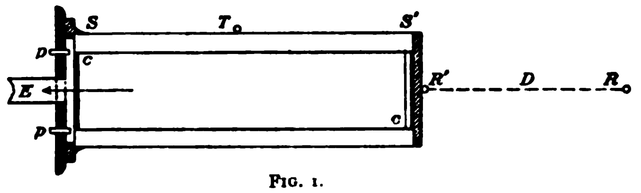

Fig. 1.

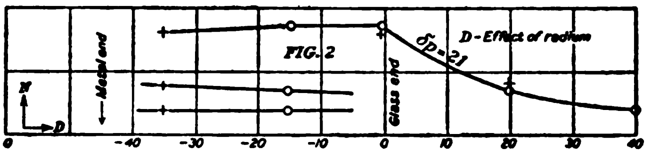

Fig. 2.

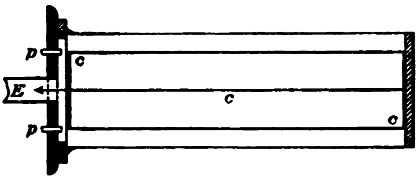

Fig. 3.

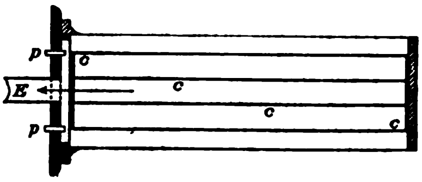

Fig. 4.

Figs. 1, 3, 4.—Types of cylindrical fog chamber. Axial section. *E*, exhaust pipe; *c*, cloth partitions.

Fig. 2.—Nucleation (N) due to weak radium at different distances from and on top (side of cylinder) of the fog chamber. Table 1.

The table gives evidence of a small difference between N^1 and N^2, but this is here unquestionably an observational error, particularly as its sign is often reversed. The chart (fig. 2) then shows the mean number of nuclei within, when the radium is at $D = 0$, 20, and 40 cm. from the end; and while the nucleation drops off rapidly from 100 to 45 and 24 per cent, respectively, the nucleation within is about constant throughout the 45 cm. of length of cylinder. At least an internal drop to less than one-fourth is out of the question, as the diagram shows. It must be remembered that the nucleation is produced instantly to saturation, that all nucleation will vanish with the removal of the radium to infinity within a few seconds, and that the ions here in question are relatively large nuclei as compared with the colloidal nuclei of dust-free air. The latter, moreover, are quite ineffective at the observed pressure difference, $\delta p = 21$, used. If larger pressure differences appear the results are usually quite different.

3. Explanation.—To account for these remarkable results is difficult. Convection is probably out of the question, though it will be quite eliminated in the following experiments. One may hazard the suggestion that the effective agency outside of the cylinder are the gamma-rays directly, whereas within the cylinder the ionization produced by those rays secondarily is in question. In other words, the gamma-rays do not act here directly, but the nuclei are produced by corpuscles set free by these rays. The medium within the cylinder is thus in a state resembling an electrolytic medium having the same ionic pressure throughout. It is this ionic pressure depending on the density and speed of the corpuscles which is transmitted instantaneously from end to end of the cylinder. To refer to the phenomenon as diffusion would be obscure without a statement as to what diffuses. The ionic nucleus is relatively a fixture and could not diffuse, in the time specified, to the far end of the cylinder, quite apart from decay.

4. Further experiments with radium. High exhaustions.—In the preceding experiments the wet cloth partition was about 10 cm. above the surface of the water below. In the new chamber shown in fig. 3, the distance has been reduced to 5 cm. Under these circumstances a very marked gradation of the number of efficient nuclei was observed for the first time. This is not, however, due to the supposed elimination of convection, but rather to the large pressure difference applied in the experiments. The result follows in table 2. When the radium tube is placed at T (fig. 1) symmetrically on the side, the metal cap virtually becomes the source of nuclei, or better, it seems to become secondarily active more intensely than the remainder of the glass chamber. The coronas obtained with two goniometers at distances 11 and 36 cm. from the brass end and 35 and 10 cm. from the glass end are rapidly larger as the brass end is approached. The ratios of the n-values is greater than 2:5. These conditions are retained indefinitely so long as the radium is present, showing that the result is not incidental. As both ends of the chamber were about equidistant from the radium, it would appear to be the excess of the secondary radiation from the metal cap which is in question.

Table 2.—Distribution of nucleation within the glass fog chamber (as in table 1) and allied results.

	s.	$N\times10^{-3}$.	$N\times10^{-3}$.
I. Radium tube on side of glass fog chamber. Two goniometers, I at 11 cm. and II at 36 cm. from brass cap, 46 cm. from glass end. $\delta p=26.0$ cm.			
No. I	6.6	95	147
No. II	4.7	38	59
[1] No. I	6.6	95	147
No. II	4.4	30	46
II. Radium on glass end, 1 cm. thick; observation I at 10 cm. and II at 35 cm. from end. $\delta p=26$.			
No. I	60	76	118
No. II	47	38	59
III. Radium at ∞. Lapse 10ᵐ.			
26.5	3.2	11	17.4
30.8	[2] 7.4	114	195
IV. Radium on brass plate, 1 cm. thick.			
30.6	4.0	24	42

[1] Three hours later no interference.

[2] w r g.

5. The same, continued. X-rays.—After finding that the fleeting nucleation within the fog chamber was unequally distributed under the excitation of radium, similar experiments were tried with the X-rays, using the fog chamber (fig. 4) with four horizontal wet cloth partitions 2 to 3 cm. apart to obviate convection. The results given in the first part of the following table are definitely affirmative. When the X-ray bulb is near the fog chamber, the nucleation nearer the bulb is decidedly in excess. Thus when the line of sight is 30 and 50 cm. from the anticathode, the farther nucleation is about 60 per cent of the nearer.

If, however, the bulb is relatively far away ($D=100$ or 200 cm.), the end of the fog chamber *farthest* from the bulb and *near* the brass cap is more actively ionized. In other words, under these circumstances the secondary radiation from the brass cap predominates. The nucleation at 10 and 30 cm. from the latter shows a decrement of 20 per cent, for instance, passing continuously from the high to the lower values. This experiment throws light on the function of the walls in producing distributions in case of persistent nuclei. Obviously the effect of secondary radiation decreases rapidly as the distance from the walls increases. The nucleation within the fog chamber is probably largely due to this kind of radiation.

6. The same, continued. Miscellaneous tests.—In the second part of table 3, experiments with radium are resumed for comparison. The gradation of number, decreasing from the brass end to the glass end, for a symmetrical position of the radium tube at *T*, fig. 1, is very marked, as usual; while the case for radium at *R*, fig. 1, again shows the largest coronas at the end of the tube, the distribution being more nearly uniform. Thereafter the radium was placed in positions *S*, *T*, *S'*, on top, successively, with the results for *T* graded about as usual. Radium at *S* still evokes gradation, but the coronas are even much smaller than when the radium is placed on the thick glass end at *R*. When radium is placed at *S'* near the glass end gradation is nearly absent, but the coronas are again small. The results are therefore not as simple as was anticipated and do not admit of an explanation merely in terms of the glass penetrated.

TABLE 3.—Distribution of ions within glass fog chamber. Metallic (brass) cap at one end, glass end opposite 1 cm. thick. Lines of sight 10 cm. (s_{10}) and 30 cm. (s_{30}) from brass end, 15 cm. and 35 cm. from glass end. X-rays acting from distance *D*.

Lead case.	*D*.	s_{10}.	s_{30}.	$N_{10}\times 10^{-3}$.	$N_{30}\times 10^{-3}$.	δp.
	cm.					
I off..................	15	G B P	W P cor	130	156	24.5
	15	w P cor	w r g	180	255	30
	15	w P cor	w o g	180	300	30
	1	w P cor	w o g	180	300	30
	[1]100	6.9 w o	6.3 w g	121	91	30
	[1]200	6.5	6.1	102	84	30
II off:						
On middle of side at *T*.	...	6.8	5.4	114	63	30
		6.6	5.0	106	48	30
On glass end at *R*...	...	5.6	5.2	69	56	30
On side near cap at *S*.	...	4.4	3.3	33	14	30
On middle of side at *T*.	...	6.4	4.5	96	36	30
On side near glass end at S^1............	...	4.8	4.8	45	45	30

[1] Large coronas near brass cap. Secondary radiation preponderating.

When the radium tube is attached to the glass end (about 1 cm. thick), similar gradations are observed, but this time with the large coronas near the radium tube. (See fig. 5.) The ratio of *n*-values is now about 2 for the given distances. The law of variation is difficult to obtain in any of these cases, but when the brass end is predominatingly active, the reduction of *n*-values is nearly proportional to distance, if the usual mean values of *s* be taken together with the special observations.

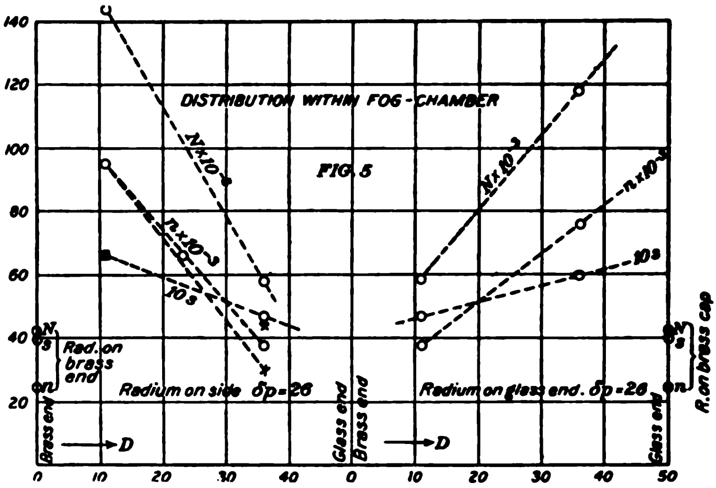

FIG. 5.—Density of ionization (N) within the fog chamber at different distances (D) from the brass end. Table 2.

In view of the action of the glass end when the radium is attached to it, it seems possible that the glass, large thicknesses of which are always penetrated and permeated obliquely by the radiation, may be active in both cases, but special inquiry is needed here. The glass cylinder was found to be thinner (about 0.15 cm.) near its equatorial parts (T), and to increase in thickness towards both ends. If, however, the phenomena were due to thickness of glass the coronas should be largest near the middle and taper down toward both ends of the fog chamber. This is not the case, as the coronas for a symmetrical position of the radium tube decrease regularly from the brass to the glass end of the apparatus.

If the radium tube is placed on the outside of the brass cap, one cm. thick or more, there is the usual moderate reduction of nucleation here, from $n=65$ to $n=24$ thousands (63 per cent); but the change of diameter of coronas within is of the same kind, decreasing from the brass to the glass end, as above.

7. Distance effects of radium.—To throw further light on present and preceding questions at issue, I shall next anticipate some of the work below and describe certain experiments specially adapted for the purpose. By "dust-free air" I mean atmospheric air filtered with extreme slowness (through large wide filters of packed cotton) and thereafter left without interference for two or more hours. Such air shows a high fog limit. In the fog chamber used the condensation began at an observed pressure difference of about $\delta p = 26$ cm.; rain-like condensation at $\delta p = 21$ cm.

In the present experiments all tests are made at $\delta p = 41.5$ cm., at a pressure difference therefore much above the fog limit, and probably approaching the condensing power of the apparatus. The number of nuclei computed from the coronas observed is an estimate merely, as the constants needed for the very large range of variation in question are not available. Nevertheless if the same δp is used throughout, the nucleations obtained are immediately comparable. With these reservations the number of nuclei found in the dust-free air and at the δp in question is about $N = 380 \times 10^3$ to 400×10^3, per cubic centimeter. It is obvious, moreover, that these nuclei are excessively small, much smaller than ions, smaller even than those which would respond to smaller δp's exceeding $\delta p = 26$ cm.

Let the fog chamber (fig. 1) be subjected to the radiations from weak radium (10,000×, 10 mg.) contained in a thin hermetically sealed aluminum tube. As the walls of the fog chamber are 0.1 to 0.3 cm. thick and the end (bottom) toward the tube nearly 1 cm. thick, γ-rays only will penetrate into the inside, apart from the secondary radiation there produced. As shown in fig. 1 (cylindrical fog chamber) the radium tube *R* is at an axial distance *D* from the nearer end. In addition to this the radium was also tested at *T* (top) in the figure, where it is nearest the body of dust-free air under experiment.

The data investigated are shown in table 5 and in the curve (fig. 6), where the abscissas are the distances *D* and the ordinates the number of efficient nuclei per cubic centimeter.

It follows from the graph that as the radium is brought in an axial direction from ∞ to the end of the fog chamber, the number of efficient nuclei in the dust-free air contained is gradually but enormously reduced to a minimum for $D = 25$ cm. (about), after which the number again increases to the maximum at $D = 0$. Curiously enough, when the radium was further approached to the body of the air by being placed at *T*, the mean number of nuclei did not increase.*

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*This result is to be further interpreted in special experiments below.

If the radium is inclosed in a long, thick lead tube (60 cm. long, walls 0.5 cm. thick), the nucleation is but moderately reduced (see crosses in fig. 6), showing that gamma-rays are in question.

TABLE 4.—Radium effect at high pressure differences. $\partial p = 41.5$ cm.; s (air) = 7.5; D, distance from end of fog chamber.

D.	s.	$n \times 10^{-3}$.	D.	s.	$n \times 10^{-3}$.
On top..	3.9	27	50	4.8	51
	3.9	27		4.9	54
25......	3.3	16	100	6.3	104
	3.4	17		6.8	129
0.......	4.8	51	∞	7.5	160
	4.7	48	End	4.8	51
On top..	4.0	27		4.7	48
	4.1	31	Top	4.6	44
0.......	4.4	37		4.7	48
	4.7	48	End	4.7	48
25......	3.3	16	Top	4.7	48
[1]0.......	4.1	31	[2]End	4.7	48
On top..	4.0	27	∞	6.1	97
[1]On top..	3.9	27			

[1] Radium tube in lead pipe walls 5 cm. thick.

[2] Lead radiation.

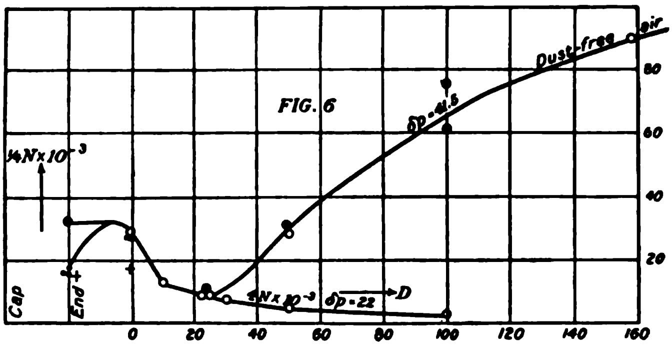


FIG. 6.—Efficient nucleation (N) near the middle of the fog chamber, for different distances (D) of radium from the end and for different exhaustions (∂p). Table 4.

8. Cause of the minimum and the maximum.—This is easily explained, since the ions are relatively large bodies and relatively few in number as compared with the nuclei of dust-free air for the same ∂p. Hence the ions capture the moisture more and more fully as their number, with diminishing distance D, becomes greater. At $D = 25$ cm. probably the whole of the moisture is condensed on ions, and as their number increases as D vanishes the minimum in question results. In fact, it was shown elsewhere that below the fog limit of air, the nucleation observed and due purely to radium at different distances, *D*, is, for example ($\delta p = 22$),

D..........	0	10	30	50	100
$N \times 10^{-3}$....	120	50	32	20	12 etc.,

agreeing in character as far as may be expected with the data here in question. These data multiplied by 4 (in other words $4n \times 10^{-3}$) are also given in fig. 6 for comparison. Hence the ions caught at $\delta p = 41.5$ are about four times more numerous than at $\delta p = 22$, and correspondingly smaller. They behave, therefore, as if they were markedly graded, but nevertheless, as a group, throughout much smaller than the nuclei of dust-free air so long as the radiant field is appreciable. While the number of nuclei continually grows smaller, with diminishing *D*, the efficient nuclei may nevertheless increase again below a certain *D*, seeing that the colloidal nuclei in dust-free air are enormously in excess, only a few of which are caught even in the absence of radium.

TABLE 5.—Distance effect of radium. *D* measured from side. $\delta p = 35$ cm.

D.	*s*.	$n \times 10^{-3}$.	$n \times 10^{-3}$.
cm.	*cm.*		
250	[1]7.6	160	300
200	[2]7.6	150	285
150	[2]7.6	145	270
100	[3]7.3	136	255
50	[4]5.1	56	105
25	4.4	35	66
12	4.2	30	57
0	4.7	45	84
Radium at ∞. Lapses 15^s and 3^m.			
∞	4.1	27	51
∞	[1]7.6	160	300

[1] GBP. [2] gyog′. [3] wog. [4] wrg.

It would be more difficult to account for the result that the same nucleation is observed wherever the radium touches the outside of the elongated fog chamber. In otherwords, radium at the end of the chamber in the earlier experiments seemed to produce the same mean nucleation as when at the top, although the distances from the center of mass of the glass are as 3 to 1; but the above experiments have already suggested that this result was probably an incidental case.

9. Further experiments with radium.—Incidental experiments corresponding to those of the preceding section are given in table 6, showing the reduction of the efficient nucleation of dust-free air when the radium tube is gradually approached to the sides of the chamber. They are shown graphically in fig. 7, both in relation to s, n, and N, and need little discussion. The minimum position lies very near the chamber and about 10 cm. from it. The action of radium is hardly perceptible beyond 1 meter, chiefly because the green-blue-purple corona happens to be involved. Sharper results could therefore be obtained at lower pressure differences, where white-red-green coronas are in question. But on the whole it is clear that radiation which appreciably lowers the asymptote corresponding to dust-free non-energized air must be of an intensity exceeding the effect of 10 mg. of weak radium (10,000 ×), at a distance of 1 meter. There does not, therefore, seem to be much hope of observing cosmical radiations in this way. Finally the second part of table 6 (and other data below) shows how soon the high nucleations of dust-free air (non-energized) is regained after the removal of the radium tube. The rapidity with which ionized nuclei fall apart is obtainable in this way and well worthy of special research. (Cf. Section 62 *et seq.*)

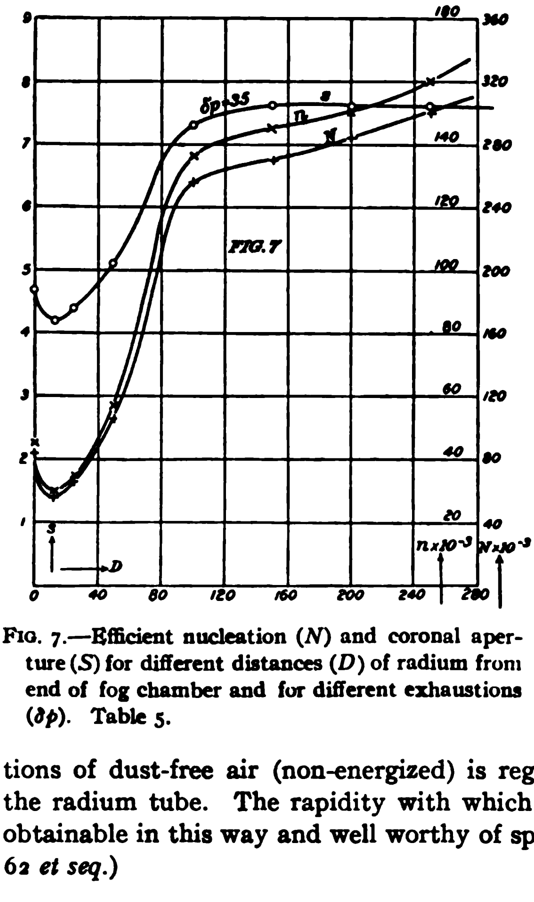


FIG. 7.—Efficient nucleation (N) and coronal aperture (S) for different distances (D) of radium from end of fog chamber and for different exhaustions (δp). Table 5.

10. Distance effect of penetrating X-radiation.—The question at issue was whether the rays which have penetrated lead are characterized by the same marked distance effect which is observed for radium. The fog chamber was inclosed in a close-fitting lead casket with two narrow side-windows for observation. The end of the casket toward the bulb was provided with a lid to be opened or closed at pleasure. When the distance is $D=50$, about 8 per cent of the radiation passes through; when $D=10$ cm. the amount is about 17 per cent. Unfortunately the observation through the window is not satisfactory and no doubt a certain amount of radiation enters here secondarily. It is therefore difficult to carry out the comparison.

TABLE 6.—Penetration through lead. Lead-cased glass fog chamber. Plates of lead 0.14 cm. thick. $\delta p=24.5$.

Lead case—	*D.*	*s.*	$n \times 10^{-3}$.
On; end closed	50	2.7	6.7
		3.1	9.5
On; end open	50	g B P.	100
On; end closed	10	3.8	19.5
On; end closed	10	3.5	16.5
On; end closed	10	3.5	16.5
Off; plate only	15	w o g 7.0	104
Off; no plate	15	g B P to	130
		w P cor.	156

Large coronas near brass cap. Secondary radiation.

11. General inferences.—The occurrence of a continuous succession of groups or gradations of nuclei in the curve of figs. 6 and 7, each of which groups constitutes a condition of chemical equilibrium for the given radiating environment, is suggestive. In the first place, it may be recalled that the nuclei of dust-free air are an essential part of this body as much as the molecules themselves. Such nuclei, if withdrawn by precipitation, are at once restored. Again, air left without interference for days shows a maximum of this nucleation for the given conditions of exhaustion when all foreign nucleation must have vanished. Indeed, the water molecules themselves may be treated as a continuous part of the nucleation in question, the frequency of occurrence being a maximum for the molecular dimensions. It is best, however, to reserve discussion for a later paragraph (section 43).

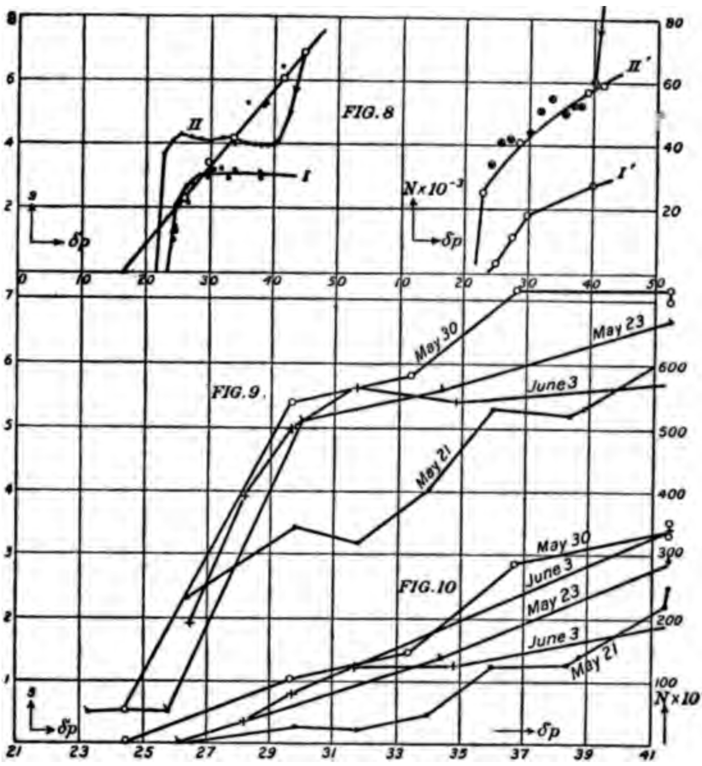
THE NUCLEATION OF FILTERED AIR IN RELATION TO DIFFERENT SUPERSATURATIONS OF WATER VAPOR.

12. Successive series of results.—Before proceeding with an account of the change of the efficient colloidal nucleation of atmospheric air in the lapse of time and other like problems, it is expedient to consider the behavior of filtered air when subjected to different exhaustions. I will proceed chronologically, taking the earliest experiments first. These may be given with sufficient detail in a chart like figure 8, in which the lower graph (I) shows the data obtained in the earlier memoirs with a wooden fog chamber. The observed pressure differences (supersaturations) are laid off horizontally, the apertures of the coronas ($s = \phi/30$, nearly, where ϕ is the angular radius to the outside of the first ring, when the eye and the source of light are at distances 85 and 250 cm. on opposite sides of the fog chamber) and the nucleations vertically. No particular attention was given to the occurrence of rain, and the measurements cease at the lower end with the measurably visible coronas. It is seen that the curve very soon reaches an asymptote, showing hopelessly poor efficiency. As the work was carefully done, the only explanation would seem to be that the speed of filtration was insufficiently slow and the exhaustion insufficiently rapid (small vacuum chamber). The same remarks apply to the graph (figure 8, II), obtained in a decreasing march of pressure difference, at the beginning of the work with the glass fog chamber (fig. 1); but the asymptote is higher. The fog limit in this case is lower and attributable to nuclei which have entered unobserved, as it is much below the values for more carefully filtered air. The first observation, having been made with the apparatus at rest for 12 or more hours, shows a very high but probably more nearly correct result.

Figure 8 also contains the corresponding nucleations, N, so far as they can be computed, supposing that the nuclei are removed faster than they can be restored. For high pressure differences the data are necessarily estimates. Naturally the differences between the data obtained after long waiting (12 hours or more), and those obtained in succession after intervening intervals of a few minutes, are enormously accentuated.

It follows from these results that if normal data were to be reached it would in the first place be necessary to perfect the method of filtration. This was done by providing the filter with a very fine screw stopcock, by which the rate of flow through the filter could be diminished very gradually to a vanishing value.

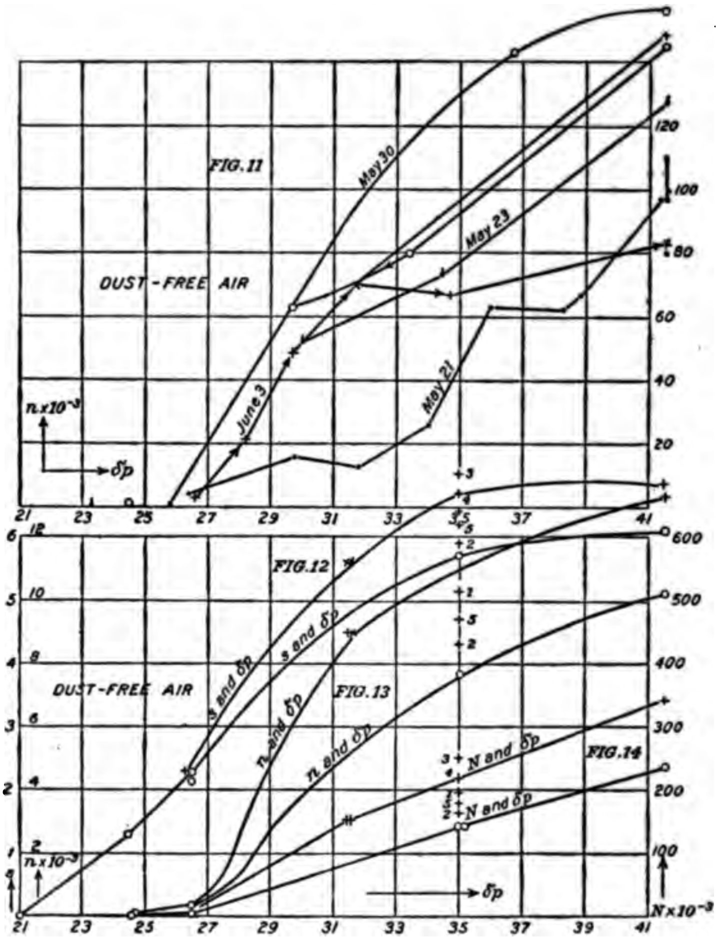
The next group of results, obtained on May 21, 23, and 30, and on June 3, were found under conditions of very slow filtration. They are sufficiently reproduced in the graphs (figs. 9, 10, 11), in which the abscissas are the pressure differences and the ordinates the coronal diameters (s) and the nucleations (n and N), respectively, as specified. The graphs for s are perhaps most suitable for discussion, although s exhibits the small nucleations with very great advantage. The data for May 21 are in the main much above those in fig. 8, but they are still far too low and irregular. The other data are much larger and as far as $\delta p = 30$ lie sufficiently near together to show that limiting conditions are being approached. Beyond this the curves diverge widely. The highest results reached are those of May 30. On June 3 a change takes place during the course of the experiment, as the result of which the incoming and outgoing curves differ. In all cases there is a distinct tendency to approach a limit after δp exceeds 37 cm., due to the limitations of the apparatus.



Figs. 8, 9, and 10.—Early data of efficient nucleations (N, n) and coronal diameter (s), appearing at different exhaustions (δp) in dust-free air. Imperfect fog chamber.

The characteristic feature of all the nucleation curves is the rapid increase between $\delta p = 27$ and 30 cm.; that is, during the early coronal stages. Below this the relatively large nuclei are present at least as far as $\delta p = 21$ to the extent of a few thousand per cubic centimeter. Nevertheless, it is their variation which brings about the sinuous outline of the curves above $\delta p = 33$, seeing that large nuclei are overshadowingly effective.

On the 5th and 6th of August a series of experiments was made to test the effect of long and short lapses of time between the observations, as well as the displacements of lower limits of the curves. The results of August 6 at $\delta p = 35$ show that 15 minutes was an insufficient time between observations, but that intervals exceeding 30 minutes (very slow filtration presupposed) are liable to show the true efficient nucleation at the time of experiment. Direct experiments made under conditions show that intervals of from one to two hours will in all cases be sufficient for the decay of extraneous nuclei.



FIGS. 11, 12, 13, and 14.—Early data of efficient nucleations (N, n) and coronal diameter (s), appearing at different exhaustions (δp) in dust-free air. Imperfect fog chamber.

Table 7.—Nucleation of dust-free, non-energized and energized air, different exhaustions, δp. Lapse about 15 min. Barometer, 75.97 cm. Piping and stopcock of 1-inch gas pipe.

δp.	s.	$n \times 10^{-3}$.	$N \times 10^{-3}$.
I. Dust-free air not energized.			
35.1	6.2	94	180
26.0	2	2.7	3.9
26.3	2.3	3.8	5.8
24.2	1.2	1.4	2.1
22.6	(?)	(?)	(?)
22.6	[1].5	.2	.3
21.0	[2].0	.0	.0
II. Radium on middle of side of fog chamber.			
21.0	3.3	11	15
19.0	(?)	(?)	(?)
19.0	[1].5	.2	.3
20.1	2.1	2.5	3.4
22.4	4.8	37	53
24.1	4.9	41	61
26.0	5.2	52	80
30.0	5.2	55	93
35.0	5.1	56	106
III. Dust-free air.			
35.0	6.2	94	180
33.0	5.8	80	143
31.1	5.5	68	117
29.3	5.2	54	91
27.6	3.1	10	16
28.1	3.8	21	34
26.3	2.1	3	4.7
28.1	3.8	21	34
29.6	4.7	41	70
31.2	5.3	60	103
33.1	5.8	80	143
35.2	[3]5.8	82	155
IV. X-ray bulb. $D = 100$ cm.; fronting bottom.[4]			
42.0	[5]7.0	146	338
41.4	[5]7.0	145	332
35.0	[5]7.0	134	255
30.7	[5]7.2	131	222
26.2	6.5	94	146
24.0	6.2	79	113
IV (continued). X-ray bulb. $D = 100$ cm.; fronting bottom.[4]			
22.7	5.6	59	85
20.9	4.9	37	53
18.8	[6]?.9	.9	?1.1
19.0	?1.0	.9	?1.2
19.0	1.2	1.2	1.6
V. X-ray bulb. $D = 50$ cm.			
19.0	1.2	1.2	1.7
VI. X-ray bulb. $D = 25$ cm.			
19.2	1.7	1.8	2.4
19.2	[7]1.3	1.3	1.8
18.2	.0	.0	.0
18.2	.0	.0	.0
VII. $D = 50$ cm. above[8] fog chamber.			
19.0	1.2	1.2	1.6
19.9	2.9	6.7	9.1
20.9	4.4	26	36
21.3	5.6	54	77
22.7	5.8	63	91
24.4	wrg 7.3	117	175
26.2	wog′ 7.8	130	200
27.7	wo′g 7.8	135	217
29.8	gBP 8.3	150	249
[9]33.0	gBP	156	281
34.9	gBP	160	303
38.3	gBP	167	346
42.0	wog′ 7.9	?174	?400
VIII. $D = 600$ cm. from end.			
35.0	[10]4.4	35	67
33.7	4.6	41	75
31.0	4.6	40	68
28.0	4.6	37	60
25.8	4.6	36	56
24.2	4.6	35	52
22.7	4.3	26	38
20.9	3.0	7.7	11
19.7	1.3	1.3	1.8

[1] Vanishing at once and faint, only just visible.

[2] Nothing (fog or rain) observed.

[3] Accidental slow reopening: same result.

[4] Exposure 2 minutes. No increment of N results.

[5] All large w r g coronas.

[6] Coronas clear but too small.

[7] Bottom of glass 1 cm. thick, interferes with formation of persistent nuclei even at short distances like 25 cm. $= D$.

[8] Persistent nuclei just begin to be generated. $s < 0.5$ cm. maximum for fleeting nuclei.

[9] Next day.

[10] Smaller than air coronas; s always taken.

13. Effect of X-rays and gamma-rays. Data.—To interpret the above results it will be necessary to vary the nucleations of the dust-free air artificially, by acting on it from the outside of the chamber with the X-rays, or with the gamma-rays of radium.

In these experiments the glass fog chamber (fig. 1), rigorously free from leakage, was used with a framework of wet cloth within. Filtration was throughout excessively slow and all other precautions were taken. The radium in the hermetically sealed aluminum tube was pasted to the top of the fog chamber at *T*. The X-ray bulb was adjustable, so as to act from different positions at distances *D*.

Table 8 shows results where δp is the pressure difference, $s/30$ the angular coronal diameter, when the distances of the eye and the lamp are 35 cm. and 300 cm. from the fog chamber. The small distances *D* (35 cm.) enabled the observer to see even the smallest coronas distinctly. The nucleation n is obtained by supposing that the nuclei are restored faster than they can be removed by exhaustion. In case of N this is not the case, so that the correction for volume expansion is added. For high pressure differences the absolute numbers are not trustworthy, but the data given nevertheless show the relations satisfactorily.

TABLE 8.—Persistent nuclei. Exposure 2^m. *D* measured from anticathode to top of fog chamber. Thick (1 mm.) aluminum screen (earthed) interposed.

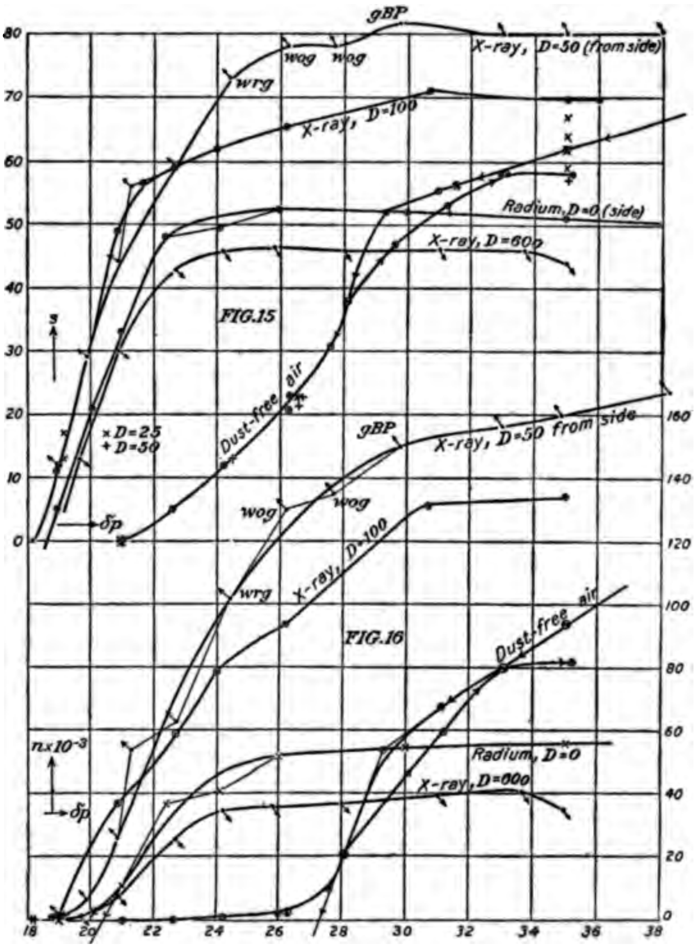
D.	δp.	s.	$N \times 10^{-3}$.	Lp.	D.	δp.	s.	$N \times 10^{-3}$.	Lp.
cm.	*cm.*			*min.*	*cm.*	*cm.*			*min.*
12	18.0	7.8	140	0	30	18.2	3.0	9	1
20	18.6	5.3	56	0		18.2	3.2	12	0
	18.4	5.7	67	1	50	18.4	.0	0	0
30	18.0	2	....	0	40	18.3	2.7	7.2	1
	18.0	[1]4.0	22	1		18.0	1.0	1.2	1
	17.5	3.0	9	2		18.0	1.0	1.2	1
	18.2	2.7	7	0	50	18.0	[2].5	.1	2
	18.2	[1]3.1	10	1		....	.5	.1	1

[1] Spontaneous generation.

[2] Just visible before falling.

The data of table 8 are constructed in the charts, figs. 15 to 17, showing the s, n, and N curves in succession, for increasing supersaturations. They will be useful for comparison with the advanced work below.

14. Persistent nuclei.—Table 8 gives the corresponding data for persistent nuclei. Distances are here measured from the sides of the fog chamber where the glass was thinner (about 0.2 cm.) than at the end (1 cm.). No persistent nuclei were obtained when the radiation passed through the end of the fog chamber as in table 7. To guard against direct inductive action the fog chamber was covered with an earthed plate of aluminum, 0.5 mm. thick, though this precaution is superfluous. The table shows the distance (D) of the anticathode above



FIGS. 15 and 16.—Early data of efficient nucleations (N, n) and coronal diameter (s), appearing at different exhaustions (δp) in dust-free air. Imperfect fog chamber. (Illustrating table 7.)

the fog chamber, the coronal diameter ($s/30$), the nucleation (N; n would have no meaning here), and the time elapsing (Lp), after the radiations are cut off until the observations are made. The time of exposure was uniformly 2 minutes. Longer exposures would have produced seriously distorted coronas. These data are constructed in fig. 18, the *s* values being dotted and the *N* values drawn in full.

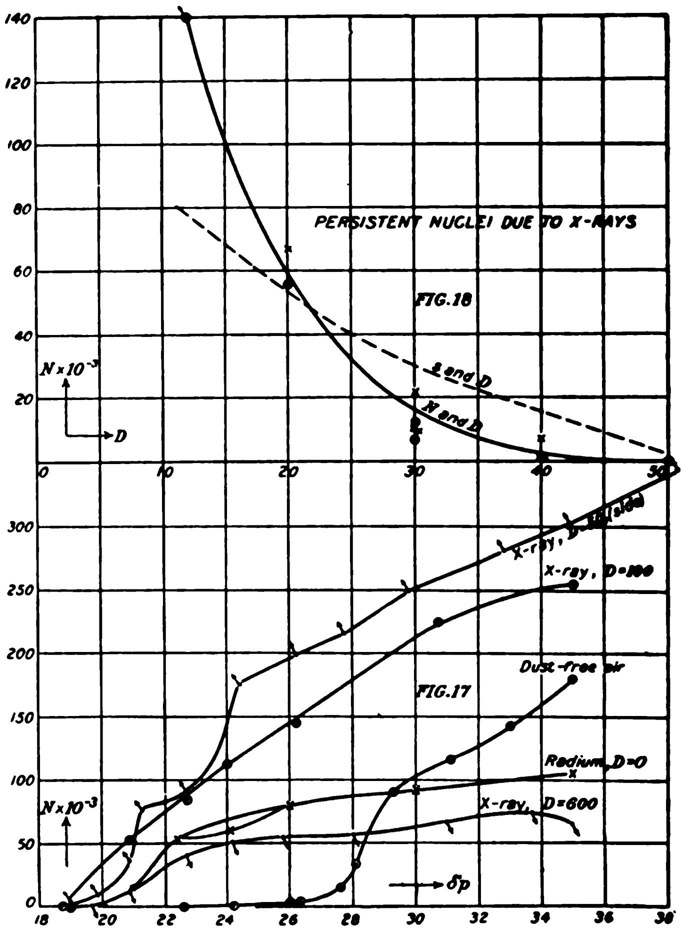


FIG. 17.—Nucleation (N) for different exhaustions (δp) and radiations. Bulb distance.

FIG. 18.—Persistent nucleation (N) produced by X-rays acting from different distances (D) from the glass fog chamber. Table 9.

15. Persistent nuclei generated through tin plate.—In view of the ease with which the cylindrical fog chambers may be made rigorously air-tight, it seemed worth while to endeavor to produce persistent nuclei through a plate of tinned sheet-iron, 0.03 cm. thick and 14 by 20 inches square. In the following trials exposures for 2 minutes to the

X-ray bulb, at a distance of about 12 cm. between the anticathode and the glass wall (0.3 cm. thick) of the fog chamber, are in question. The earthed iron plate was placed between bulb and chamber, resting on the latter. A lapse of time of 1 minute was allowed after the radiation had been cut off. This suffices to show that nuclei of the persistent kind have been entrapped. Naturally the pressure difference used precipitated no appreciable fog in the absence of radiation.

These results show conclusively that persistent nuclei may be produced through earthed tin plate, provided the thickness used is not excessive.

TABLE 9.—Persistent nuclei through earthed tinned iron plate, 0.03 cm. $\delta p = 25$ cm., practically below fog limit. Exposure to X-rays, 2 minutes; lapse, 1 minute; observation during exposure.

X-rays—	s.	$n \times 10^{-3}$.
On............	2.0	2.5
Off	.0	.0
On............	2.0	2.5
Off............	.0	.0
On............	[1]Weak	....

[1] $\delta p = 24.5$; corona too faint for measurement, but definitely present.

16. Discussion.—The simplest of the graphs are those of figure 18, showing the decrease of persistent nuclei as the bulb is gradually removed (D increasing and measured from the side of the chamber) from the apparatus. This decrease is very rapid and implies that if the anticathode were actually in contact with the glass walls the production of persistent nuclei in 2 minutes would be enormous. The distortion of the coronas resulting under these circumstances, as detailed in the last memoir, is not, therefore, surprising. It should be remembered that the rays have to penetrate more than 2 mm. of glass. On the whole the action is very much like what C. T. R. Wilson describes for ultraviolet light.

As in the earlier case, there is *secondary generation; i.e.*, the number of nuclei is larger if the observations are made at 1 or 2 minutes or more after the radiation has been cut off.

With the given apparatus, persistent nuclei were still produced for a distance of 0.5 meter between the X-ray bulb and fog chamber, though the coronas in that case were but just discernible and vanished too rapidly for measurement. The corresponding intensity of ionization is then near the point of transition from persistent to fleeting nuclei, a result which will presently be made use of.

The pressure difference ($\delta p = 18$ cm.) used throughout is (for the given apparatus) far below the fog limit for dust-free air ($\delta p = 21$ to 26).

In case of the fleeting nuclei or ions, the generation is instantaneous and it will be necessary to represent the data (s, n, N) for a continuous series of supersaturations for each of the five intensities of ionization applied, beginning with non-energized dust-free air. These are given for both increasing and decreasing values of δp, the latter being at times larger (as would be expected from the removal of larger groups on condensation); but on the whole the data are very satisfactory.

Remembering that the number is roughly as the cube root of s, the region of ions ($\delta p = 21$ to 26) is particularly well represented. They increase slowly but regularly in number until the coronal stages are reached. Beyond these the increase is again slow; but that it is real is shown by the top curve for X-ray nuclei, which fails to ascend.

The lowest pressure at which the suggestion of a corona could be observed in the given apparatus was $\delta p = 21$ cm. The coronal fog limit is best found from the other curves.

The succeeding curves (X-ray, $D = 600$; radium, $D = 0$; X-ray, $D = 100$, 50, 25 from end and 50 cm. from side) correspond to gradually increasing ionization. It may be noticed that the fog limits slowly move to the left into smaller supersaturations, while the initial slope of the curves gradually rises. Persistence sets in when the slope is nearest the vertical. All the curves eventually approach a limit, which for weak radiation is practically reached near the fog limit of air, but for strong radiation much beyond it. In the upper curves the green-blue-purple corona first appears at $\delta p = 30$ cm. It is noteworthy that the asymptote is reached later as the ionization is stronger.

The relation of these results as to numbers of nuclei is best shown by the n-curves, fig. 16, though the scale is now too small for the ions of non-energized air. In this case (n) it is assumed that the nuclei are reproduced faster than they can be removed by expansion. The curves throughout have the same characteristic, being doubly inflected and showing definite stages in which nucleation increases most rapidly. If these branches are prolonged backwards the coronal fog limit may be specified for each, as shown in the figures. This quantity decreases at a retarded rate, while the ionization grows more intense.

The effect of weak ionization (radium, or X-ray at $D = 600$) is to increase the number of ions. It has been supposed above that the result of this is to mask the corresponding increase of any of the colloidal nuclei originally present, should such an increase occur.

The curves, moreover, throw important light on the distance effect D. Thus at $\delta p=22$, the effect of increasing D from 1 to 6 meters is a fall of n from 50,000 to 20,000—about 60 per cent. At $\delta p=30$ the fall is from 130,000 to 40,000—about 69 per cent. Owing to the uncertainties of observation these numbers may possibly be the same, in which case the gradation of size of the nuclei would be the same for all intensities of ionization.

The initially slow increase of the upper curves ($D=50$ cm.) is possibly due to the formation of persistent nuclei, as stated at the beginning of this section, these capturing much of the moisture.

Finally, the evidence given by the N curves, fig. 17 (assuming that the nucleation is not restored faster than it can be removed by the exhaustions), is much the same as that just detailed. The curves are often straighter than heretofore, and continually rise as the result of the increasing volume expansion; but the double inflection remains. In fact, the rise of all the upper curves is eventually at about the same rate as for air. In the latter case the scale is again too small to show the increase in the region of ions.

At $\delta p=22$ the distance effect for 1 and 6 meters is a decrease of 60 per cent, at $\delta p=30$ a decrease of 71 per cent, naturally nearly the same as above.

Both the N and n curves show that while within the limits of observation intense radiation increases the nucleation of dust-free air, this is not the case for weak ionization. Here the curves cross at about $\delta p=29$ cm. Above this the presence of radiation must decrease the efficient nucleation of non-energized dust-free air; below this it will increase it. At high pressure differences like $\delta p=41$ cm., as used below, the variation of the efficient nucleation must therefore be a sensitive criterion for the variation of the ionization of air. Similarly the direct experiments of sections 7 and 9 find their explanation in the manner already pointed out.

17. More rapid exhaustion. Apparatus and data.—The preceding set of experiments correspond to the particular exhaustion cock used. This was an inch plug gas cock. As almost the whole resistance to flow was encountered here, the advisability of enlarging it seemed evident. In fact, on opening the cock suddenly to an amount corresponding respectively to about 1/4, 1/2, 3/4, 1/1, the nucleations obtained were about $N\times10^{-3}=40$, 100, 180, 350 for $\delta p=41$ cm., showing that not even an approach to the limit is reached in the extreme case. There is a further objection in having the large resistance in the stopcock, as the coronas will vary with the degree of opening.

TABLE 10.—Nucleation of dust-free air, energized or not. New apparatus, 1½-inch stopcock; connections of inch gas pipe. Barometer 76.23 cm. Walls of fog chamber 0.3 cm. thick. Three horizontal wet cloth partitions within chamber.

δp.	s.	$n \times 10^{-3}$.	$N \times 10^{-3}$.
I.			
44	[1]7.7	180	440
42	[1]7.6	175	400
	7.6	175	400
	7.6	175	400
35	[1]7.6	160	300
	7.6	160	300
30.8	[2]7.5	137	235
26.1	2.6	62	9.7
24.3	.7	.2	.4
	.5	.1	.2
25.3	1.4	1.7	2.6
26.1	2.6	6.2	9.7
27.0	3.6	17	27.5
27.6	5.0	46	75
28.6	5.4	60	99
29.3	6.3	92	153
30.5	7.0	125	212
35.0	[1]7.7	160	300
35.0	[1]7.8	160	300
30.5	[2]7.5	136	230
II. Radium tube added on side. Barometer 76.05 cm. (Mean values.)			
43.6	4.4	40	95
35.0	5.4	67	126
30.8	5.6	69	120
26.4	5.6	64	97
24.2	5.6	60	87
22.8	5.6	57	87
21.2	5.6	55	74
20.0	4.1	20	28
18.8	0	0	0
19.0	0	0	0
19.0	.5	.1	.1
19.6	2.6	5.2	6.9
20.4	4.9	37	51
21.0	5.2	43	60
III. X-rays. $D = 50$ cm. from side.			
48.9	[3]7.6	190	560
43.6	[4]8.0	216	530
III (continued). X-rays. $D = 50$ cm. from side.			
35.2	[6]9.0	240	450
30.8	[6]9.3	258	440
26.6	[6]9.2	229	360
22.8	[8]8.0	137	200
21.5	[8]7.3	120	170
20.8	[6]7.2	100	138
19.5	5.1	39	52
18.6	1.1	1	1
18.3	?0	?0	?0
IV. X-rays. $D = 12$ cm. from side.			
18.9	2.2	2.7	3.7
20.0	5.7	54	74
21.0	[8]7.4	117	165
23.0	[7]7.3	125	180
24.5	[6]9.5	195	290
29.3	[8]10.5	290	490
35.0	[8]10.7	320	610
43.7	[6]10.3	306	750
52.2	[4]9.4	240	760
V. Dust-free air. Fog chamber with 4-sheeted wet cloth. 2 to 3 cm. apart. Barometer 76.36 cm.			
28.8	5.1	....	....
27.0	3.4	....	....
25.3	?.0	....	....
25.8	2.1	....	....
25.3	?.0	....	....
25.8	2.3	....	....
	2.1	....	....
	2.3	....	....
30.8	[8]7.3	....	....
31.6	[8]7.4	....	....
32.3	([9])	....	....
33.1	[6]7.7	....	....
34.0	[9]7.8	....	....

[1] g′BP corona steadily repeated, but not quite clear. [2] wog. [3] GBP. [4] wP corona. [5] wrg. [6] wyg. [7] gyog′. [8] wog′. [9] Vague.

Accordingly the inch stopcock was replaced by a 1½-inch plug gas cock, retaining the same inch tubing. The resistance in this case was least at the stopcock, which accounts for the remarkable steadiness of the results obtained in successive exhaustions.

Furthermore, the fog chamber was modified by inserting three wet cloth partitions, horizontal and about 5 cm. apart, as shown in fig. 3. The new form was not merely favorable to better saturation, but all convection currents were more effectually cut off. This was at first (though incorrectly) supposed to be the reason for the appearance of distributions of nuclei within the chamber produced by the action of radium kept outside of it, a result already detailed above, but which here appeared for the first time in a very marked degree. In the later experiments four cloth partitions were inserted, as in fig. 4.

The results are given in the successive parts, table 10, in the usual way, dust-free air being examined with and without the interference of external radiation. It is not probable that any errors are now introduced by the filter.

In view of the intense ionization used, the usual cycle of measurable coronas is exceeded, and the resulting data become more and more fully relative, both on this account and because of the high pressure differences applied. Absolute values are, however, of little interest, and it is precisely from the relations obtained that conclusions are to be drawn. The quantities s, n, N, δp have been frequently defined. D is measured from the side of the apparatus, so that all action takes place through 0.3 cm. of glass. No aluminum screen was interposed.

18. Remarks on the *s*-curves. Non-energized air.—The present *s*-curves for non-energized air, fig. 19, are in strong contrast with the preceding. Variability in the lapse of time has been nearly eliminated. The curves have moved bodily somewhat farther to the left into the region of smaller supersaturations, as is shown by comparison with the dotted line in fig. 19 (taken from the preceding fig. 15), evidencing the increase of efficiency referred to. The curves of fig. 19 are in remarkable contrast with the preceding in two respects; they reach a definite asymptote at about $\delta p = 35$, which is retained until the pressure difference is so high that other complications step in. There is certainly an increment after $\delta p = 30$, as proved by the change of coronas. Whether this limit is due to a cessation of further drop of temperature in the apparatus, or whether a distinct group of colloidal air nuclei is in question, remains to be seen. The possibility of the continued succession of groups of this kind is not, *a priori*, improbable.

19. The same, continued.—The other characteristic, which was entirely unforeseen, is the relative absence in what has been called the ionized region (placed in the former curves, fig. 15, between about $\delta p = 21$ and $\delta p = 26$). The contrast is clearly shown in fig. 19. The only explanation which suggests itself to me is this, that what were supposed to be ions were really water nuclei due to the somewhat slower exhaustion of the preceding experiment. In other words, particles caught at the end of the somewhat less rapid expansion evaporated into the larger particles, leaving water nuclei behind. But apart from this, the definite trend with which the curve reaches the abscissa is characteristic, and, so far as coronas go, there seems to be an absence of nuclei below $\delta p = 24$. In other words, the fog limit has been raised, in spite of the general lowering of the necessary supersaturations throughout the curve. The new curve is almost wholly coronal.

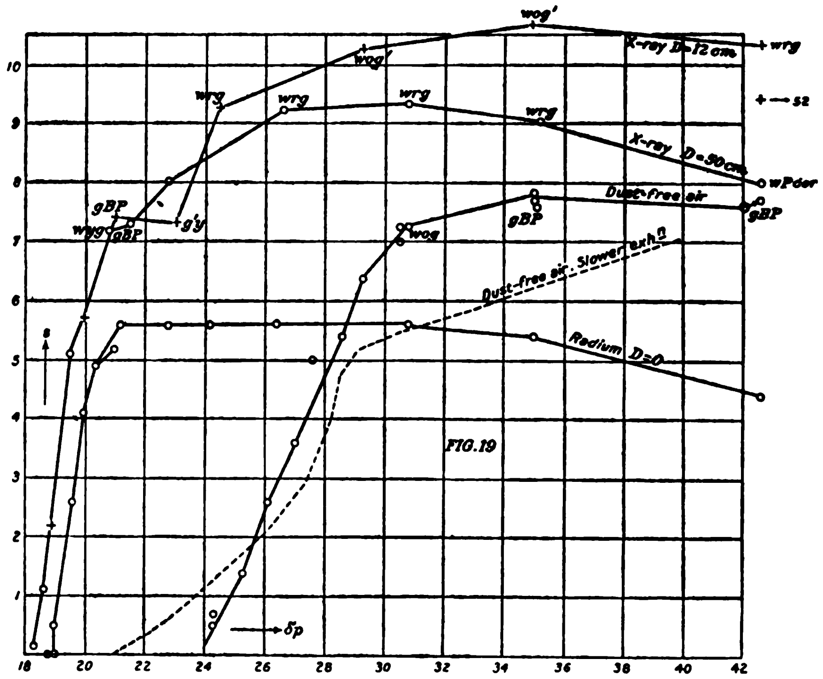


FIG. 19.—Improved fog chamber. Apertures of coronas (s) seen in dust-free air, energized or not, as stated, by radium or X-rays, at different exhaustions (δp). Table 10.

Usually the same results are obtained in a pressure-increasing and in a pressure-decreasing series. There is an equally striking uniformity in the lapse of time.

20. The same, continued. Action of radium.—The action of radium is characterized by a slight rise of the asymptote over the preceding case and of displacement of the curve into smaller supersaturations. This was to be anticipated; nuclei are caught more easily, and a somewhat smaller order of size and increased number is detected in consequence. The other distinctive feature is the smaller range of pressure differences within which practically all condensation occurs. In the preceding experiments this range lay between $\delta p = 18$ and 24, whereas in the present case the marked changes fall between $\delta p = 19$ and 21. There results another apparent rise of the fog limit corresponding to the coronal effects, though it is slight and uncertain. What is noteworthy is the greater steepness of the rising branch of the curve, already indicated. The question may be asked whether for a rigorously instantaneous exhaustion this part of the curve would become even more nearly vertical. One may note that the radium curve eventually passes through a maximum. Furthermore, while in its initial stages it lies very near the former X-ray curve ($D = 50$), the latter shows no tendency to reach a near asymptote.

21. The same. Action of X-rays.—Finally, the results with the X-rays are similar. High asymptotes, a tendency of the curve to lie within a region of lower supersaturations than in table 7, etc., are apparent. Nuclei smaller in size and larger in number have been caught more easily than heretofore. If we regard the present and the earlier curves for $D = 50$, the height of asymptote in the former case is much above the one in the latter case, and moreover passes through the maximum (reached at $\delta p = 26$) as δp increases indefinitely. This corresponds to the result for radium.

It is therefore interesting that if the radiation is further intensified, as in the last case, where $D = 12$ cm., the curve continues to rise apparently throughout higher ranges of pressure. The limits are not reached (δp continually increasing) until nuclei of a size equal in smallness to the order holding for the colloidal nuclei of air have become available for condensation. A final point deserving comment is the break of the X-ray curve near $\delta p = 22$. This is not only marked in both curves of table 10, but similarly apparent in table 7. Unfortunately, the cycle of coronas changes at this point (green-blue-purple corona); but apart from this it seems probable that with intense X-ray radiation, two successive groups of nuclei are in question; the first group prominent below $\delta p = 22$ and the second above $\delta p = 22$.

22. Remarks on the *n*-curves. Non-energized air.—The *n*-curves, which assume that the nuclei are replaced sooner than they can be removed by exhaustion, bring out the points just made with better regard to the actual nucleation, seeing that the *s*-curves are specially favorable to small numbers of nuclei. As a rule the new nucleations obtained are nearly twice as large as the old results. It seems probable that the upper inflection, after passing the nearly straight part, is due to the waning condensing power of the apparatus, and that in the absence of this loss of efficiency the middle region of the doubly inflected curve would continue indefinitely. One may note, too, that both in case of tables 7 and 10 the parts in question are nearly parallel, or that the increment of nucleation corresponding to a given increment of super-

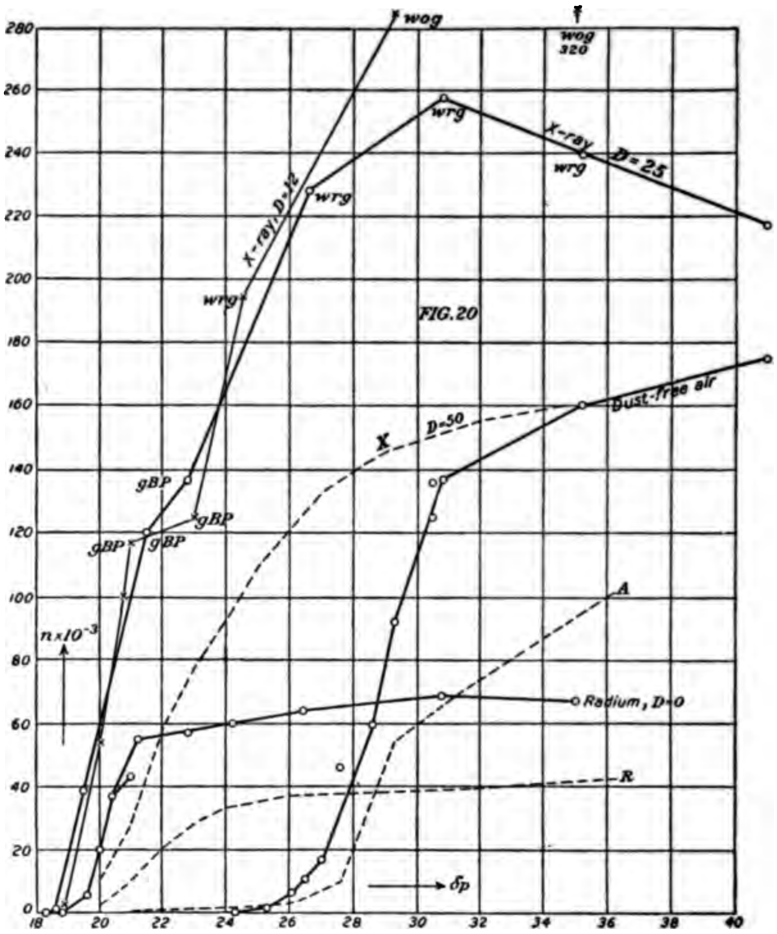


FIG. 20.—Improved fog chamber. Efficient nucleation (*n*) free air corresponding to fig. 19. Table 10.

saturation is about the same. This applies even in the following cases, where dust-free air is energized by radium and by intense X-radiation, as far as the middle regions of the curve are concerned.

23. The same. Action of radium.—The small increment of pressure difference (say $\delta p = 19$ to 21) is here in sharp contrast to the gradual increase observed in the old results (say between $\delta p = 19$ and 25). The nucleations which eventually are not quite doubled in the new results, as compared with the older, are therefore at first enormously in excess. In fig. 20 the results of table 10 are given in full, the old results (table 7) in broken lines, and the same method is pursued in the other cases.

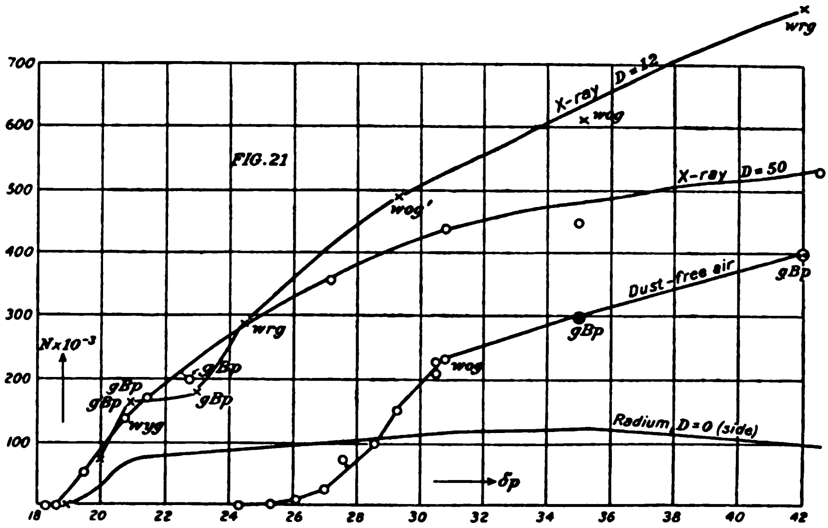


FIG. 21.—Efficient nucleation (N) in dust-free air corresponding to fig. 19. Table 10.

24. The same. Action of X-rays.—Remarks to the same effect may be made with reference to the old and the new data for X-ray ionization when $D = 50$ (broken and full lines in fig. 20). Initially the old curve is even below the present curve for radium, but it eventually intersects the new data for dust-free air at about $\delta p = 35$. The mean nucleations have not been quite doubled. The maxima in cases of $D = 50$ and $D = 12$ lie above the interval of large variation for dust-free air. Finally, the breaks in the curves at $\delta p = 22$ are again quite apparent.

25. Remarks on the N-curves.—With regard to the N-curves, fig. 21, one need merely note that the maxima have in most cases been definitely wiped out, and that the nucleation available for condensation, if it be supposed that removal of nuclei is more rapid than the reproduction, increases continually with the supersaturation up to the highest values.

THE NUCLEATION OF FILTERED AIR IN THE LAPSE OF TIME.

26. Method.—In the above experiments with filtered air, it has been carefully pointed out that all the curves tend to reach asymptotes, the height of which depends on the other (larger) nuclei present. If, then, the ionization of dust-free air is an essentially variable quantity, as shown by the electrometer, the height of the asymptote in question should be correspondingly variable.

Again, it was shown that external radiation (gamma-rays of radium for instance) are powerful nucleators, whether directly or secondarily. Hence external radiation of this type, if variable, might be reasonably sought for in a study of the nucleation of dust-free air.

In relation to the ordinary intensities of radiation, this method of varying asymptotes is exceedingly sensitive. Whether, however, it will apply for cases of much weaker (cosmical) radiation must be left to experiment. Moreover, whether the variable ionization of air can be detected in the manner suggested, or whether it even exists in the fog chamber, is similarly a question requiring experimental solution.

27. Early data.—The method here in question was carried out in a series of experiments begun May 9 and continued until September 2, 1905. In the earlier part of the work it was shown that comparable results could only be expected in cases of excessively slow filtration, the filters for this purpose being 18 inches long, 2 inches or more in diameter, and containing cotton very tightly packed. It was necessary, moreover, to make observations after long intervals (12 to 24 hours) of waiting, the object being to allow all nuclei which might have passed through the filter time to decay. Apparent variations of considerable interest were obtained in this way; but the work below will show them to have been untrustworthy. Neither changes of temperature nor of the barometer produced any effect.

To additionally safeguard the work, two fog chambers were eventually installed side by side, drawn upon by the same exhaustion system identically in every way. It was then found that the internal partitions of wet cloth were essential, but it was nevertheless impossible to make both chambers agree even when the partitions were increased fourfold. Throughout the work, nucleations passing through maxima and minima within the limits of about 400,000 and 160,000 were obtained, apparently under trustworthy conditions. The data remained consistent even when the fog chambers were exchanged. Small variations of the rate of filtration were quite ineffective, showing that a limit has been reached.

28. Apparatus modified.—The tubing of the preceding apparatus, which consisted of inch plug cock and inch gas pipe, was now taken apart and a 1½-inch brass plug cock was substituted. The advantage of this arrangement is easily seen, inasmuch as the whole resistance to flow is practically in the pipes. The passage-way in the stopcock being larger in area, the rate of exhaustion obtained is independent of slight differences in opening.

As a result of this, all the variations noted above practically disappeared, and the nucleations of dust-free air at a given pressure difference were found to be constant in the lapse of time within the limits of accuracy of the method. Data of this character are shown in the following table:

TABLE 11.—Nucleation in the lapse of time. $\delta p = 30.6$ cm. w o g′; $n \times 10^{-3} = 127$; $N \times 10^{-3} = 227$.

Date.	Corona.	*s.*	Date.	Corona.	*s.*
Sept. 5[1]	w o g	7.4	Sept. 12	w o g	....
6	w o g	7.4	13	w o g	7
7	w o g	7.4	14	w o g	7.2
8	w o g	7.4	15	w o g	7
9	w o g	7.4	16	w o g[3]	7.1
9[2]	w o g	7.3	18	w o g	7.2
10	w y ʻg	7.4	20	w o g	....
11	w o g?	....	21	w o g	7.2

[1] Apparatus with three sheets.
[2] Apparatus with four sheets.
[3] Apparatus with one sheet, 10 cm. above surface of water.

Indeed, the succession of different fog chambers with 1, 2, and 3 cloth partitions all gave the same results. The rate of filtration could be varied without effect within wide limits, and the same corona was obtained after a few minutes or after 24 hours of waiting.

29. Inferences.—It has, therefore, not been possible to detect changes of nucleation, either as the result of the concomitant changes of atmospheric ionization or as the possible result of some form of cosmical or at least external radiation. The consistency of the results obtained for radiation under widely different conditions may be especially pointed out. It does not follow, however, that other methods (not depending on the terminal asymptote) may not be more efficient. In how far this is the case will be shown in Chapter VI.

SUMMARY OF THE RESULTS OF THE CHAPTER.

30. Distribution of ions within the fog chamber.—Within the fog chamber, the coronas due to the ions produced either by radium or by the X-rays acting axially from long distances, as a rule vary in aperture from one end of the long vessel to the other. Hence the distribution of nuclei is not uniform in the direction of the axis of the fog chamber. The reason for this is to be ascribed to secondary radiation. As interpreted from the nucleation produced within the fog chamber containing dust-free moist air, dense bodies (brass cap) produce more secondary radiation than rare bodies (glass end) under like conditions of primary radiation.

If the primary radiation is relatively intense, rare bodies like glass may produce more secondary radiation than dense bodies (like the metals) under less intense primary radiation; or at least the decrement of primary radiation with the distance from the source predominates within the fog chamber.

The secondary radiation is rapidly absorbed by the air, as the diminishing coronas testify.

31. Minimum of efficient nucleation.—When ions and colloidal nuclei are in presence of each other (or in general any two groups of nuclei of different average size), the number of efficient nuclei for the case of a drop of pressure not too small passes through a well-defined minimum, if the number of ions continually increases from zero. This occurs, for instance, when a radium tube is moved from a long distance quite up to the fog chamber. The ions abstract more and more of the available moisture, until the colloidal nuclei are practically inactive (minimum), after which the nucleation increases again with the number of ions.

32. Persistent nuclei.—For the moderately intense X-ray bulb (5-inch spark) and a glass fog chamber several millimeters thick, persistent nuclei may be demonstrably produced when the distance from bulb to chamber increases to about 50 cm. They may even be produced through thin tin plate. The decrease with distance of the number generated within a given time is very rapid, and the number producible if the anticathode could touch the fog chamber would be enormous. In like manner the number increases at an accelerated rate with time of exposure as if the nuclei were themselves active.

If we regard the ionized state of a gas as characterized by a kind of kinetic ionization pressure, we may further conceive the ionized gas to be subject to something resembling saturation, whereby ions pass into persistent nuclei when the ionization pressure reaches a certain limit very much as a vapor condenses.

33. Dependence of efficiency of fog chamber on the size of the exhaust pipes.—If a (long) cylindrical fog chamber, whose contents are not much in excess of 6,000 c. cm., be exhausted into a vacuum chamber whose contents exceed 100,000 c. cm., through a passage-way 50 cm. in length and about 2.5 cm. in bore, many of the experiments showing the properties of ions and of the colloidal nuclei of dust-free air are consistently producible, provided the plug exhaustion stopcock (opened quite and as quickly as possible) has a wider bore than the pipes. With exhaust pipes of this size, however, the apparatus is as yet very far from its limits of efficiency, and the largest or terminal corona obtainable in case of the colloidal nucleation of dust-free air is, even at the highest exhaustion, the intermediate green-blue-purple type. This leaves the whole order of large coronas outstanding, though the order may be entered if the air is intensely ionized. It follows that efficiency actually stops short because of the smallness of the colloidal nuclei.

The curves showing the nucleation entrapped in case of continually increasing exhaustion all have a common feature; there is an initial low branch of small variation attributable to ions; an intermediate branch showing steep ascent, due to colloidal nuclei; a final asymptotic branch, corresponding to the terminal corona and due to the loss of efficiency of the apparatus. The middle branch in question, or line of representative colloidal nuclei, if it appears at all, has almost the same slope and position (relative to the field as a whole) for all fog chambers, whether their efficiency be small or great. The fog chamber ceases to act almost abruptly; in other words, the terminal corona or largest corona producible as the drop of pressure continually increases, appears in any fog chamber as an almost sudden departure from the representative lines. This corona is larger or smaller, the asymptote higher or lower, as the fog chamber is more or less efficient.

34. Invariable character of colloidal nucleation in the lapse of time.—The terminal corona (in a given type of apparatus), if not too small (Chapter VI), is a fixture as to size in the lapse of time (months). It does not vary appreciably with the departure from normal ionization, to which atmospheric air is incident. Probably the number of available colloidal nuclei is too enormous, as compared with the small variations in number of the relatively large ions, to admit of an observable effect.

CHAPTER II.

LATER AND FINAL STAGES IN THE EFFICIENCY OF THE FOG CHAMBER DUE TO A GRADUAL INCREASE IN THE BORE OF THE EXHAUST PIPES.

CONNECTING PIPES NOT LARGER THAN 1.5 INCHES IN DIAMETER.

35. Introductory.—It will be the object of the present chapter to further determine to what an extent a perfectly efficient apparatus (*i. e.*, one in which the cooling and the moisture precipitated per cubic centimeter actually accords with the drop in pressure) may be approached by gradually enlarging the bore of the escape pipes between the vacuum chamber and the fog chamber. One method of doing this will consist in finding whether the distribution curves eventually reach a fixed limit and a limit maintained for larger as well as smaller nuclei; another by comparing the final results with corresponding data deduced for Wilson's piston apparatus.

In treating the large numbers of observations which follow, it will be convenient to refer the nucleations (as above) to the drop of pressure observed under *apparently* isothermal conditions at the fog chamber. This method of comparison is sufficient if the same fog and vacuum chambers are used throughout, as has actually been done in the sequel. The exhaust cock is always to be closed immediately after exhaustion. In the present experiments the volume ratio of the two vessels was about $v/V=0.064$, where v is the volume of the fog chamber and V that of the vacuum chamber.

It was customary, as just stated, to open the stopcock between the fog chamber and the vacuum chamber as rapidly as possible and then to close it at once; δp therefore denotes the drop of pressure read off on the mercury gage at the fog chamber after sufficient waiting. As above, s is the angular diameter of the coronas on a goniometer radius of 30 cm., when the eye and the source of light are respectively 40 cm. and 250 cm. on opposite sides of the fog chamber. On the basis of these data n is computed from the quantity* of water precipitated per cubic centimeter and the value s, in the way shown elsewhere.† It is always assumed that the nuclei are more rapidly reproduced than removed by the exhaustion, or (without hypothesis) from another point of view, that the nucleation of the *exhausted* fog chamber is specified. Otherwise it would be necessary to multiply by the ratio of volumes after and before exhaustion.

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* Wilson: Phil. Trans. Roy. Soc. London, vol. 189, 1897, p. 298.

† Smithsonian Contributions, vol. XXXIV, No. 1651, 1905, chap. viii.

Diagrams of the apparatus used have already been given in Chapter II (figs. 1 to 4), and further examples will be shown of the details of the more perfected forms below (figs. 26, 34, 64). In those paragraphs, moreover, I will treat the corrections to be applied (which are much larger than were anticipated) in order to pass from the *observed* apparent δp to the true values. These must be computed from the volume ratio of the two chambers and their respective initial and their final isothermal pressures when in communication.

36. Examples of data for 1-inch connecting pipes.—These were about 18 inches or more in length and the stopcock inserted was 1½ inches in bore, as specified in the preceding chapter. The plug was as usual floated in paraffin oil, absolutely preventing the influx of atmospheric air, though some leakage (which is generally harmless) from the fog chamber to the vacuum chamber could not be prevented. The fog chamber in these exhaustions had a rather larger charge of water than usual, a circumstance to which the higher fog limits may possibly be due, since these vary with the volume ratio.

TABLE 12.—Pipes 1 inch, cock 1½ inches. Non-energized dust-free air. October 24.

δp.	s.	$n \times 10^{-3}$.
30.6	7.4	139
28.9	5.8	74
27.2	4.2	26
25.7	1.5	1.9
24.6	...	0

The results are to be shown below (fig. 22, p. 37) in comparison with the later values and may be passed over here.

37. Data for pipes 1.5 inches in diameter.—Fog chamber and vacuum chamber were now connected by brass gas pipes 1½ inches in diameter and 2 feet long, and the plug stopcock interposed was 2 inches in bore. In the case of table 13 the disposition of apparatus was such as to require the length of piping specified with an elbow. The results are given in the usual way and show a distinct gain in efficiency over the earlier set in table 13, proving that greater width of pipe is still an advantage.

TABLE 13.—Nucleation of dust-free air, energized or not, as stated, at different supersaturations. Plug gas cock, 2 inches; piping 1½ inches in bore, 2 feet long.

δp.	s.	$n \times 10^{-3}$.
I. Non-energized air.		
cm.	*cm.*	
30.7	[1]7.2	151
28.2	5.9	77
26.3	3.7	19.7
24.4	2.7	6.8
22.4	2.3	3.3
20.3	.0	.0
22.0	1.7	2.1
24.7	2.7	6.8
27.6	6.1	80
29.9	[2]7.3	135
34.2	[3]8.1	190
Non-energized air. Experiments.		
34.8	8.4	190
34.7	[4]10.0	270
34.8	[5]8.9	220
34.6	[4]10.7	270
34.5	[5]9.0	220
II. Non-energized air.		
42.1	[6]9.3	250
34.5	[7]10.5	318
32.1	[8]9.2	262
30.0	[9]8.0	150
27.9	6.1	80
26.0	3.8	20
24.3	2.7	6.7
22.5	2.0	2.3
21.1	?1.0	r
17.3	!.0	.0
18.6	!.0	.0
II (continued). Non-energized air.		
19.9	?0.8	0.6
20.4	1.2	1.2
21.0	1.6	1.7
Later.		
43.5	[7]11.2	354
47.9	[7]11.2	372
43.8	[7]10.8	338
39.1	[8]10.1	286
34.9	[10]8.9	192
30.8	[11]7.5	144
III. Air energized by radium, on side of glass fog chamber.		
21.7	6.0	67
20.9	5.7	56
20.2	5.2	42
18.6	1.0	.8
16.5	.0	.0
?18.7	1.2	?1.2
18.8	1.9	2.0
21.0	?5.7	56
20.0	5.4	47
26.4	6.8	104
24.9	6.8	100
23.5	6.8	96
22.0	6.7	89
20.0	5.4	47
29.0	6.5	99
33.2	6.0	88
38.9	5.9	91
43.6	5.7	85
IV. Air energized by X-rays[12]. $D = 20$ cm. from side of fog chamber to anticathode.		
34.7	[13]12.3	400
31.0	[13]12.3	380
26.3	[13]12.3	340
22.0	[14]10.6	207
17.6	1.4	1
16.5	.0	0
17.6	2.1	2
19.6	[15]8.1	140
19.0	4.4	24
V. X-rays. $D = 50$ cm.		
32.1	[16]11.4	310
35.0	[16]11.3	320
26.6	[14]10.7	233
22.1	[17]8.6	145
17.4	?r	0
17.7	?0	0
19.0	2.2	2.7
20.0	6.1	64
X-rays. $D = 20$ cm. after long waiting.		
34.6	[18]11.2	....

g′ B p, repeated. [2] g y o b g. [3] w p cor. [4] w v o g, after waiting one or more hours. [5] w′ P cor after waiting but a few (10 to 15) minutes. [6] w c g. [7] w o g. [8] w r g. [9] g′ B P. [10] w P cor. [11] w y cor. [12] Air non-energized, $\partial p = 34.8$; $s = 9.6$; and by X-rays. [13] w y g′ large. [14] w r g. [15] w c g. [16] w o b g. [17] w P cor. [18] g y o b g.

Long waiting before exhaustion (to remove water nuclei) is often essential. In addition to the dust-free gas, air energized by radium (10 mg. of a weak sample, 10,000×, sealed in aluminum and acting from without) and by the X-rays is treated for comparison.

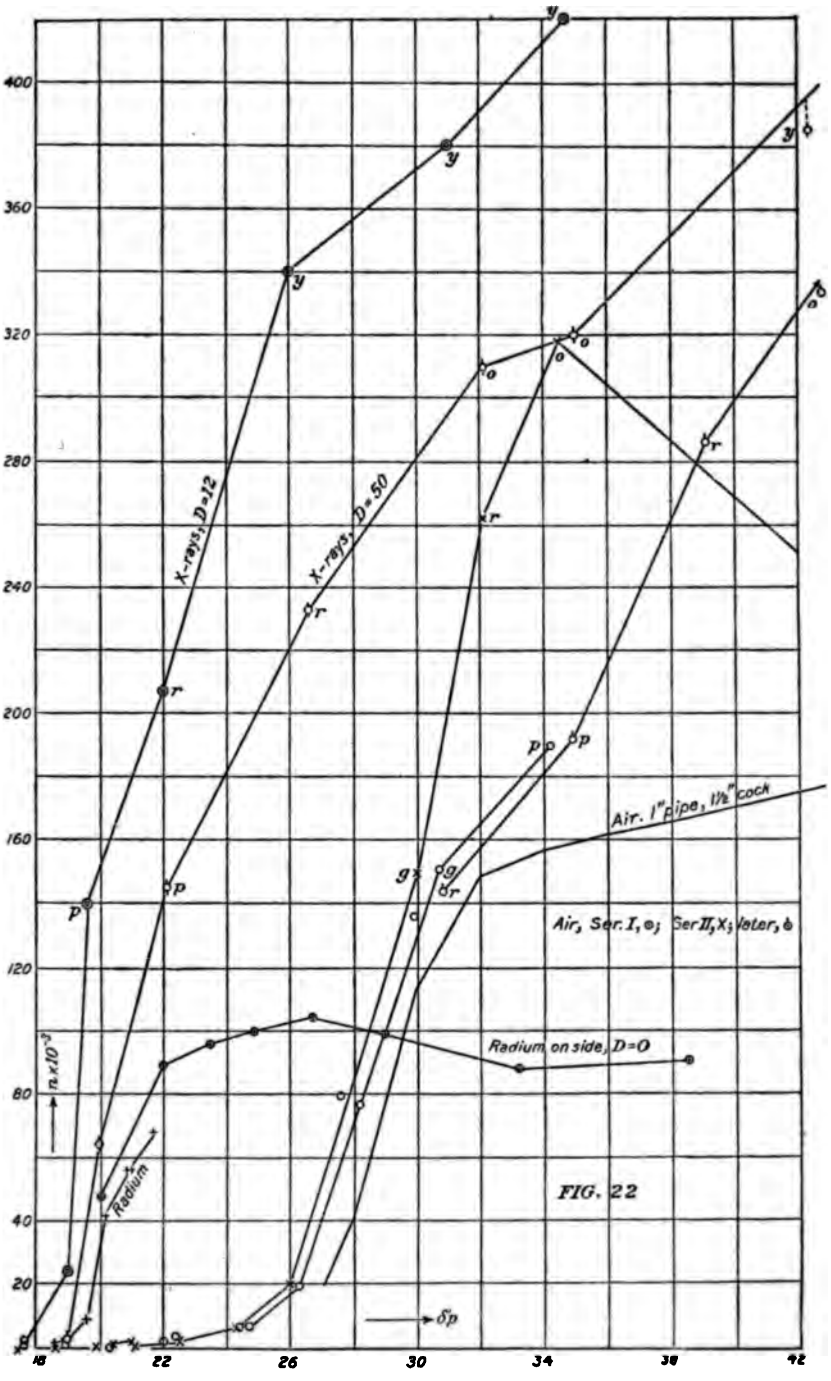

FIG. 22—Efficient nucleation (n) found in dust-free air energized or not by radium or the X-rays, as stated, from different distances (D), at different exhaustions (δp). Fog chamber with pipes 1½-inch bore, 2 feet long. Table 13.

These results, together with the data of table 12, are shown in fig. 22. For the air curve a marked advance beyond the results of table 12 is at once apparent, but it is noteworthy that the slopes of both curves are in the main the same, in spite of the fact that the former rises to but one-half or one-third of the height of the new curve. The efficiency of both fog chambers therefore terminates abruptly in a final or fixed corona or (in the chart) in an asymptote which would be horizontal, if it were not necessary to assume that the quantity of water, m, precipitated per cubic centimeter increases with the drop in pressure. In the different series, irregularities are often apparent which are difficult to explain, though at low values they may be due to cosmical radiation. Thus the second series for non-energized air rises more abruptly than the first and third, results which are possibly associated with the presence of water nuclei and referable to different degrees of leakage from fog chamber to vacuum chamber; but it is also possible that unequally rapid closing of the stopcock after exhaustion may have left an impression. The results for radium and the X-rays will reappear under better conditions presently, and may then be discussed. One may note that for weak radiation the graphs intersect the graph for non-energized air.

38. Continued. Shorter pipes.—The next step consisted in a remodeling of the apparatus, whereby shorter connecting pipes would suffice. Two 6-inch nipples, 1½ inches in diameter and containing a 2-inch plug stopcock, now joined the fog and vacuum chambers. The results are shown in table 14 and in fig. 23. The fact that the main resistance is still encountered in the gas cock is proved by the need of stops to insure quick and complete opening. Whenever the cock is nearly but not quite opened, however suddenly, low coronas are observed. When this was remedied, fixed coronas thereafter corresponded to each δp. The table contains the usual series of comparative results for air energized by radium and the X-rays.

As compared with the preceding data there is a small shifting of the graph toward lower pressures, while the slopes in the representative parts of the curves are practically the same. The terminal corona, however, and the corresponding asymptote, is markedly raised. Nevertheless, though the large green-blue-purple corona now appears in the case of strongly energized air, it has not yet been reached in the non-energized cases. The limit of efficiency is therefore not yet in sight when a fog chamber of about $v=6{,}000$ c. cm. empties into a vacuum chamber of about $V=100{,}000$ c. cm. through 30 cm. of piping about 4 cm. in diameter, with a corresponding plug stopcock suddenly opened between stops to arrest the motion.

TABLE 14.—Nucleation of dust-free air, energized or not, at different supersaturations. Plug gas cock, 2 inches; piping 1½ inches in diameter, 2 × 6 inches long. Long intervals between observations.

δp.	s.	Corona.	$n \times 10^{-3}$.
I. Non-energized air.[1]			
39.8	12.8	g y o b g	460
39.8	13.0	w y b g	420
35.1	13.0	w y g	400
30.8	10.4	w r g	260
28.6	7.4	w r g	108
27.9	5.7	w B P	69
26.0	2.4	cor	4.5
26.4	3.6	cor	17
II. Non-energized air.[1]			
24.3	1.5	cor	1.8
24.4	1.8	cor	2.1
26.2	2.6	cor	6.3
27.3	5.0	cor	46
28.0	6.4	w r g	92
29.3	7.6	g B P	139
29.5	8.0	g B P +	147
30.9	10.0	w r o g	290
30.4	8.4	w c g	230
31.2	9.1	w r g	260
35.0	11.5	w y g′	400
III. Non-energized air.			
31.0	9.8	w r o g	290
31.0	10.3	w r o g	290
31.0	[2]10.4	w r o g	290
35.3	12.0	w y b g	400
35.1	12.0	w y b g	400
39.4	12.0	w y b g	420
44.1	12.5	g y o	490
41.3	12.5	g y o	470
38.6	12.0	w y b g	420
30.7	10.2	w r g	290
IV. X-rays at $D = 20$ cm. from side.			
30.9	13.0	g B P	460
35.4	13.0	g B P	480
33.0	13.0	g B P	470
31.5	13.0	g B P	460
29.2	13.0	g B P	430
IV (continued). X-rays at $D = 20$ cm. from side.			
27.2	12.7	g y o	380
25.6	12.7	g y o	360
24.1	12.2	w y g′	320
22.8	11.9	w o g	250
29.4	12.3	g B P	440
27.1	Vague	g B P	410
20.8	7.7	....	120
23.4	11.7	w o g	250
22.9	11.4	w o g	250
21.4	8.4	g B P	120
20.2	4.6	cor	30
18.7	.0	....	0
18.3	.0	....	0
IV. X-rays. $D = 10$ cm.			
35.1	14.0	[3]g B P	480
40.3	....	g B P	510
37.9	....	g B P	500
33.6	....	g B P	470
31.6	....	g B P	460
30.0	....	g B P	450
28.1	....	g B P	430
26.7	....	g B P	410
25.0	13.5	[4]g B P	400
23.6	12.6	g y o	320
22.3	10.3	w o g	250
21.2	7.1	w o g	100
20.1	4.2	cor	21
18.7	1.3	cor	1.3
V. Air[5] energized by radium, $D = 0$, on side.			
30.8	6.1	cor	87
35.2	6.2	cor	95
40.0	5.9	cor	92
27.6	6.0	cor	79
26.2	6.1	cor	78
24.3	6.3	cor	79
22.9	6.5	cor	85
21.6	6.1	cor	68
21.0	4.7	cor	33
19.7	2.1	cor	2.5
19.2	.0	....	.0

[1] In neither series I or II were stops provided for the exhaust cock. This is the case in series III, et seq.

[2] Filter open 90° without danger. Evaporated corona shows $s = 7.6$.

[3] Coronas at first stone-blue and irregular, soon becoming g B P.

[4] Clear g B P at once.

[5] For air, $s = 9.9$ w o g. $n \times 10^{-3} = 290$. Large coronas fall out, leaving a smaller one behind.

Several interesting features are seen in the radium and X-ray curves in fig. 23, to which special attention may be called. It will be observed that the curves for distances $D = 10$ and 20 cm. of the anticathode from the sides of the fog chamber begin and terminate in nearly coincident curves and coronas, but that they lie at some distance apart in their middle regions. Hence available* nuclei are apparently not more numerous eventually in one case than in the other, but they are larger (virtually) in the middle regions for the stronger radiations; in other words, the asymptote is more quickly approached for the stronger radiation.

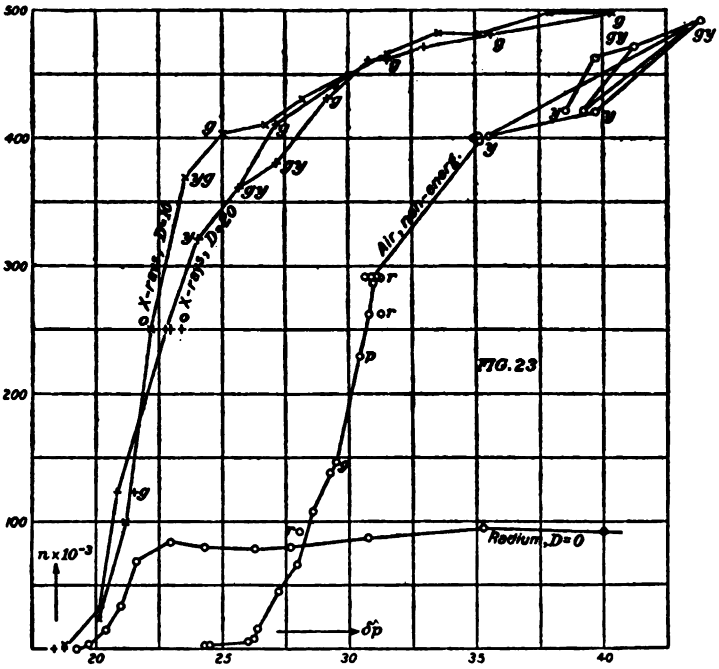

FIG. 23.—Efficient nucleations (n) in dust-free air, energized or not, as specified at different exhaustions (δp). Table 14.

Again, the terminal corona in case of the data for X-rays is reached long after the final coronas for the weak radiation from radium (10 mg. 10,000×); *i. e.*, the number of nuclei (ions) in the case of the weak radiation ceases to increase in a region of lower exhaustion, apparently, than the one observed for the more intense radiation. Hence in case of the latter, finer gradations of nuclei appear to occur, as if the radiation shattered certain of the larger ions. There is, however, another point of

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*It will appear below that for nuclei, large or small, the limit is reached with the given *number* of nuclei per cubic centimeter, corresponding to the g B P corona. Nuclei in excess of this, large or small, are inefficient.

view to which some probability may be assigned. In the case of intense radiation relatively large and possibly persistent nuclei are produced in greater numbers, and these may capture much of the moisture and prevent condensation on the smaller ions, until proportionately larger exhaustions have been applied. Examples of these occurrences will be given in the next paragraph.

CONNECTING PIPES TWO INCHES IN DIAMETER.

39. Remarks on the method.—The connection between fog chamber and vacuum chamber was now further enlarged by using two nipples 6 inches long and 2 inches in diameter, on either side of a plug stopcock of 2½ inches bore. The latter was chosen, since much of the resistance was heretofore encountered in this place. Usually observations were taken at long intervals of time apart, to allow for the dissipation of water nuclei due to the evaporation of very small fog particles. Moreover, a considerable period (three days) elapsed before definite results could be recorded. Something of a nuclei-producing character is usually present some time after assembling the parts of the apparatus. The coronas under otherwise like circumstance gradually increase to a maximum. Moreover, in the absence of all leakage inward from without, periodicity of coronal diameter is often in evidence in the successive exhaustions and especially active in case of the very large coronas. The best results appear after long waiting before each observation, whence it follows that evaporation from the heavy paraffin oil used for tightening the stopcocks, leakage of nuclei through the filter or through unknown channels is quite ineffective. Waiting was finally made needless by first exhausting the partially exhausted fog chamber before each definite observation. The effective drop of pressure is then small and only the large nuclei are caught and the fog particles do not evaporate appreciably. The filter, moreover, in all tests gives evidence of entire trustworthiness. It was customary to open and close the plug cock quickly, between stops, a spring opening device having been put in action. In no case was there danger of under-saturation, the wet cloth linings being but 8 or 10 cm. apart, above and below. In the highest exhaustions used, $\delta p = 44$ cm. about, the volume expansion is fully 2.5, so that 60 per cent of the air must thereafter be readmitted freshly through the filter. Naturally in this slow passage it would be not only denucleated but deionized, if there were not fresh sources of penetrating radiation always in action for the reproduction of both types of nuclei. In general the apparatus seems to have behaved faultlessly. Such irregularities as remain must then in large measure have been introduced by the fact that the drop of pressure was *observed* at the fog chamber when isothermal conditions had been reestablished. It should have been computed from the initial pressures of both chambers and their common isothermal pressure when in communication, in the way shown in the next section. The present results, however, suffice for comparison with the preceding and following work, and it is probable that limiting conditions of efficiency have already been reached. That this is actually the case will also be shown in the next section.

40. Data for pipes 2 inches in diameter, 12 inches long.—The results obtained are fully given in table 15. It appears that coronas, even above the large green-blue-purple type, appeared at the high exhaustions, but this is not quite certain.

Incidentally some data on the effect of X-rays from different distances are included in the tables (part VI *et seq.*). The usual difficulty of an inconstant X-ray bulb appears. Moreover, certain peculiar results on the distribution of the nuclei within the fog chamber in case of symmetrical exposure to weak radium are here again noticed (part V), as in Chapter I, section 4. The results are plotted in fig. 24 and smooth curves obtained therefrom are shown in fig. 25.

TABLE 15.—Air nucleation at different supersaturations. Piping 2 inches in diameter, 12 inches long; plug gas cock, 2½ inches in bore. Wait 30 minutes between observations. Angular diameter of coronas, $2 \sin^{-1} s/60$. Eye 40 cm., lamp 250 cm., on opposite sides of fog chamber. δp observed isothermally at the fog chamber.

δp.	s.	Corona.	$n \times 10^{-3}$.
I. Non-energized dust-free air.			
35.4	14	g B P	480
35.3	14	g B P	480
40.6	14	g B P	510
44.4	14	[1]g B P	540
41.4	14	g B P	520
36.6	14	g B P	490
33.0	14	g B P	470
31.1	....	g y o	410
29.5	10.3	w r′g	250
27.7	6.4	w r′g	91
29.3	10.4	w r g	250
28.0	6.7	w r g	104
26.2	2.6	cor	6.3
26.0	3.1	cor	9.9
24.0	1.0	cor	1.2
27.2	7.1	w y′g	120
I. Non-energized dust-free air—Cont'd.			
28.0	7.7	wPcor	170
28.9	10.6	w r o g	280
30.8	12.5	g y o	410
31.8	12.8	g y o	420
33.0	13.0	g B P	470
II. Air energized by X-rays; $D = 10$ cm.			
33.3	(2)	(3)	470
35.0	....	(3)	480
39.8	13.5	b′B P	510
31.7	....	b′B P	460
26.9	....	b′B P	420
24.5	11.5	b′B P	390
23.3	11.7	g[1]B P	380
21.0	13	w o bg	230
II. Air energized by X-rays; $D = 10$ cm.—Cont'd.			
20.4	9.0	w c g	170
21.0	11.4	w o bg	230
19.7	6.2	wr bg	190
19.1	4.1	cor	19
18.4	1.3	cor	1
17.4	.0	....	0
Continued, next day; $D = 10$ cm.			
18.5	[4]0	....	0
18.5	0	....	0
18.9	1.6	cor	2
20.3	6.8	w r g	87
20.9	9.3	w c g′	180
21.9	....	g y o	330

[1] Stone-blue colors, above g B P.

[2] Irregular. Shows strong purple band just above water. Coronas diffuse.

[3] Stone-blue.

[4] Left over night seems to diminish rainlike condensation.

TABLE 15.—Continued.

III. Air energized by X-rays; $D=60$ cm.

δp.	s.	Corona.	$n\times 10^{-3}$.
17.5	0.0	....	0
19.1	1.7	cor	2
20.3	6.1	w r g	65
21.0	8.7	w c g	180
22.5	11.7	w o g′	250
22.8	12.2	w o g′	270
23.5	[1]13.0	g y o	340
24.8	....	g y o	350
26.6	....	g y o	370
26.6	....	g y o	370
30.9	....	g y o	410
35.8	....	g y o	440

IV. Air energized by X-rays; $D=600$.

δp.	s.	Corona.	$n\times 10^{-3}$.
40.0	8.7	....	250
36.0	7.3	cor	150
31.7	6.1	cor	90
27.2	5.2	cor	52
24.4	5.2	cor	50
23.0	5.2	cor	46
21.0	5.0	cor	39
19.4	.0	....	0
19.4	.0	....	0
18.1	.0	....	0
20.3	3.1	cor	8
21.0	4.8	cor	35
23.0	5.7	cor	60
26.3	5.4	cor	57
31.0	5.8	cor	76
35.3	[2]6.9	cor	130
35.4	6.8	cor	125
39.8	8.1	w r	205
44.3	10.0	w o	322
44.4	[3]10.0	w o	322

V. Air energized by radium (10 mg. 10,000×); $D=0$, on side.

δp.	s.	Corona.	$n\times 10^{-3}$.
44.3	[4]9.7	w o′	305
40.2	7.5	w r′	153
35.9	6.6	w o	115
33.5	6.6	w r	111
30.8	6.5	w r	103
27.0	6.1	w r	79
24.4	5.8	w r	66
23.2	6.2	cor	74
20.9	5.8	cor	60
20.5	4.7	cor	32
19.4	1.3	cor	1.3
18.3	.0	....	.0

VI. Air energized by X-rays.

δp.	s.	Corona.	$n\times 10^{-3}$.
[5]22.9	5.5	w r g	55
[6]22.9	7.3	w y g	110
[7]22.9	7.7	w | BP	140
[8]22.9	9.7	w c g	200

VII. Air energized by X-rays; $D=200$ cm.

δp.	s.	Corona.	$n\times 10^{-3}$.
19.0	2.1	cor	2
20.3	6.8	w r g	85
20.9	7.4	w g	105
22.8	7.5	lgBP	125
25.9	7.5	gBP	135
31.1	7.4	w y g	135
30.4	[9]7.4	w o g	130
35.5	7.4	w o g	135
35.1	[9]7.4	w o g	135
40.0	7.4	w o g	145
43.9	7.0	wrog	135

VIII. Air energized by X-rays; $D=600$ cm.; repeated for contrast.

δp.	s.	Corona.	$n\times 10^{-3}$.
43.9	10.7	w o g	300
46.8	10.6	w o g	310
48.8	10.5	w o g	320

IX. Air energized by X-rays; $D=100$ cm.

δp.	s.	Corona.	$n\times 10^{-3}$.
44.4	7.6	w | BP	180
41.9	7.6	w | BP	170
36.2	7.6	g B P	160
31.8	7.6	g B P	150
25.4	[10]8.8	w c g′	200
26.5	9.2	w r g	205
24.0	9.3	w c g	195
21.6	8.2	w | BP	130
20.8	7.4	w y g	105
20.3	5.5	cor	50
19.7	[11]4.1	cor	19
28.0	8.8	w c g′	215
31.6	7.8	g | BP	170

X. Air energized by X-rays; $D=50$ cm. from end.

δp.	s.	Corona.	$n\times 10^{-3}$.
30.8	8.8	w r g	230
35.6	8.7	wPcor	220
40.1	8.2	wPcor	205

XI. The same; $D=50$ cm. Bulb more efficient.

δp.	s.	Corona.	$n\times 10^{-3}$.
31.6	9.8	w c g	245
27.0	10.8	wrog	235
25.2	10.9	wrog	225
22.2	10.0	w c g	200
20.3	6.1	w r g	65
35.1	9.2	w c g	240
40.0	8.3	wPcor	205
44.0	7.8	w | BP	180
48.7	7.7	g′ BP	190
32.2	10.4	wrog	260

---

[1] As intensity of ionization increases there is less shattering.

[2] Next day. Fog chamber absolutely tight. Coronas all blurred.

[3] The final use in response to new conditions.

[4] Coronas blurred and larger at the glass end of fog chamber.

[5] $D=600$ cm.

[6] $D=3{,}000$ cm.

[7] $D=150$ cm.

[8] $D=75$ cm.

[9] Long waiting (½ hour to 2 hours) without effect.

[10] Passing, as usual, through a maximum.

[11] Fog limit below 20.

41. The same, continued. X-ray bulb inclosed in lead.—In the experiments detailed the X-ray bulb was not inclosed, so that secondary radiation issued from the whole surrounding environment. In the data given in table 17 the bulb is surrounded by a wide lead box, containing a window 7.5 cm. in diameter fronting the fog chamber. The window was in a removable side or lid of the box. This was kept at a long distance ($D=600$ cm.) in order to furnish weaker ionization than was specified in table 15.

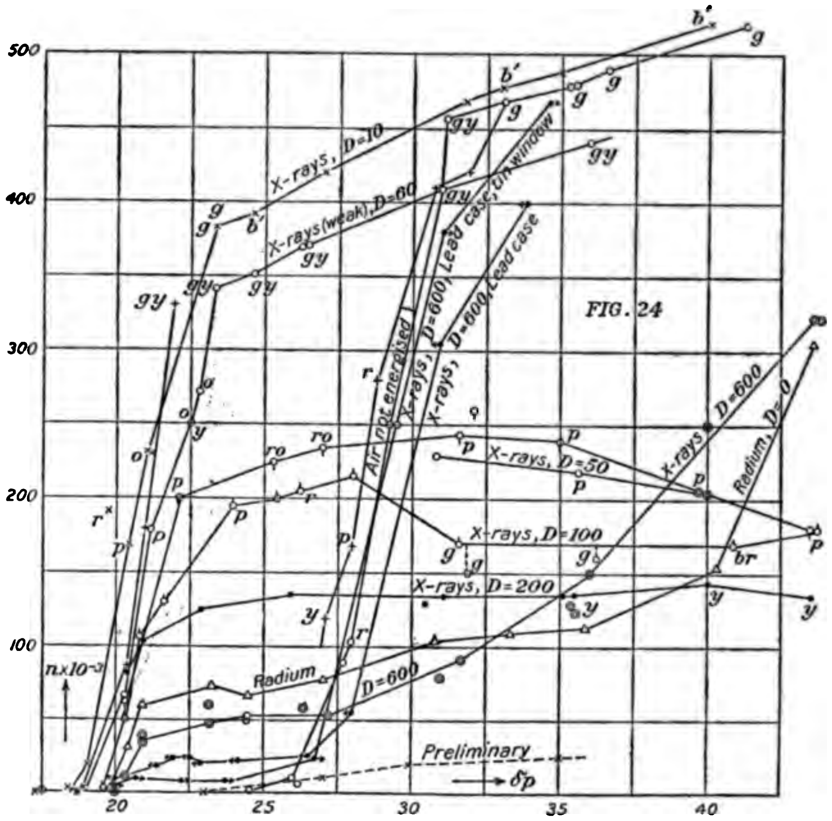

FIG. 24.—Efficient nucleations in dust-free air, energized or not by radium or the X-rays from different distances (D) and different exhaustions (δp). X-ray bulb not within lead case, unless stated.

In the first part of table 16 the exhaustion, $\delta p=27$ cm., lies below the fog limit of dust-free air. The low degree of ionization is thus shown under different conditions. The second series contains a number of successive exhaustions for an increasing δp, with the radiation passing through a thin tin plate. Parts III and IV of the table are similar series, with the window open (tin plate removed), the last series being a detail for the initial part of the curve, which is of especial interest. The results are also shown in fig. 24, where their relation to the lowest curve, $D=600$ cm., for the open or non-inclosed X-ray bulb becomes evident. In each of these curves there is a definite horizontal branch within which the ions predominate. Beyond this lies the rise due to the colloidal nuclei, but the curves, and particularly the asymptotes, are depressed in both cases.

TABLE 16.—Nucleations at different exhaustions. 2½-inch cock, 2-inch piping, 12 inches long. X-ray bulb in lead case at $D=600$ cm. from glass fog chamber. Aperture in case 7.5 cm. in diameter.

Lead box.	s.	Cor.	δp.	$n \times 10^{-3}$.
I. Window open..........	3.1	cor	20.5	8.4
Window closed with lead.	.0	cor	20.5	.0
Window open..........	3.4	cor	20.5	11.7
Window closed with tin[1].	2.9	cor	20.5	6.8
Front lead side off[2].....	3.5	cor	20.5	13.0
II. Closed with tin plate...	.0	cor	18.6	.0
	3.0	cor	20.6	7.6
	2.7	cor	22.3	6.4
	2.8	cor	23.7	7.0
	4.1	cor	26.8	24.3
	12.0	w y b g	31.2	380
		g B P	34.7	480
III. Tin plate off..........	....	[3]w y b g	33.8	400
	....	w o g	31.0	305
	5.2	w r	28.0	55
	4.2	cor	26.6	26
	4.1	cor	24.5	23
	4.2	cor	22.5	24
	3.4	cor	20.7	12
	2.6	cor	20.0	5.2
Tin plate on..........	1.7	cor	20.0	1.7
IV. Tin plate off..........	2.5	cor	20.0	4.8
	3.8	cor	21.5	17
	4.2	cor	22.0	24
	4.0	cor	22.7	20
	4.0	cor	24.0	21

[1] Open side over 1 foot square.

[2] Lead sheet 0.12 cm. thick; tin plate 0.03 cm. thick.

[3] After long waiting.

42. Discussion.—It will now be in place to make a more complete survey of the manifestations of nucleation in dust-free air under any conditions. Figs. 24 and 25 are useful for this purpose. With regard to the method I may recall that the difficulties were enhanced by the need of providing rapid exhaustions in case of a fog chamber large enough to measure the coronas and to show the sequence of axial colors.

The earliest results (Chapter I, section 12) scarcely captured the maximum of 30,000 nuclei under the extreme exhaustion corresponding to the limiting asymptote (marked "preliminary" in fig. 24). In proportion as the apparatus was perfected, this asymptote was raised, step by step, until nucleations of at least 500,000 were left in the *exhausted* fog chamber. Probably the asymptote, or more accurately the terminal corona, obtained in any given type of apparatus, indicates that the limit of condensing power has been reached. Between the fog limit and the terminal corona the graph rises in a straight upward sweep; and it is remarkable that the rates at which the nucleation decrease with the drop of pressure, or better with the volume expansion, are about the same between fog limit and asymptote, no matter whether they lie within the region of high supersaturation characteristic of the colloidal nuclei or in the region of relatively low supersaturation characteristic of ionized air. Moreover,

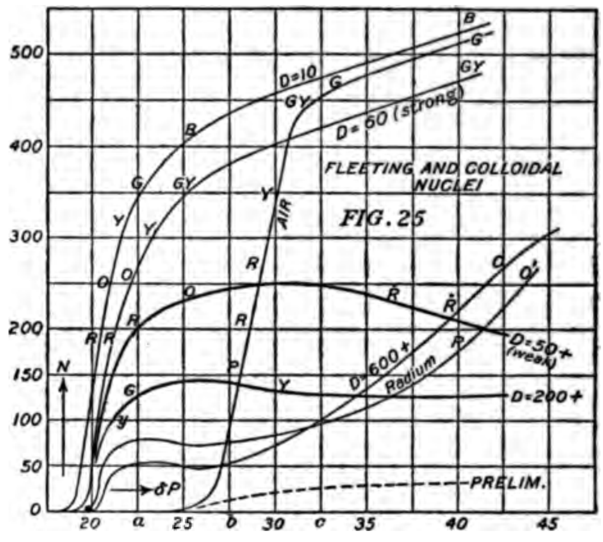

Fig. 25—Smooth curve from fig. 24. Nucleation (N) of dust-free air, in thousands of nuclei per cubic centimeter, energized or not, as stated, by weak radium, or by the X-rays, at different distances (D in cm.). The letters attached to the curves indicate the characteristic colors of the inner field (or its margin) of the largest coronas, the order of colors being R, O, Y, G, B. The abscissas show the *observed* isothermal drop of pressure by which the supersaturation is produced and the nucleations applied relatively to the given apparatus. The line marked "air" shows the behavior of dust-free non-energized air terminating in the large green coronas. In a perfect apparatus supersaturation would increase enormously beyond a; the droplets would be at freezing beyond b. In the given apparatus efficiency probably ceases beyond c when damp air is the medium.

they are the same in any apparatus, within the limits of its efficiency. In fact, even the curve which I have endeavored to reduce to the same scale from Wilson's disk colors for non-energized dust-free air (apart from differences in the meaning of δp to be explained in the next section) lies in the same region of pressure difference, and shows a slope quite in keeping with the other curves.* For an imperfect apparatus, on the other hand, the slope terminates abruptly at a lower asymptote and in a region of higher exhaustion. It will be convenient to refer to the nuclei belonging to the slopes specified as representative nuclei.

To obtain the curve for the colloidal nuclei of dust-free air, it is often necessary to wait a week or more, until unknown internal sources of nucleation have spent themselves. Moreover, the isolated observations made with advantage ought to be made hours apart, for it is with the exhaustion that the release of spurious internal nuclei occurs, suggesting that water nuclei due to the evaporation of small fog particles are possibly in question.

The air curve passes through the first two cycles of large coronas, terminating beyond the highest green-blue-purple, actually in the stone-blue or higher coronas, the first of the series producible in the fog chamber by any means whatever. It corresponds with the opaque of the steam jet, beyond which, however, there exists another cycle of yellows, to my knowledge beyond the reach of the fog chamber. It is not probable that the medium is as yet quite optically inactive after the bluish coronas specified, but merely appears so in small thicknesses.

If we turn from the curve of non-energized air to the case of *weak ionization* such as is produced by 10 mg. of impure radium (10,000×) or by the X-rays from a distance of 6 meters, we may note in the first place that the coronal fog limit has enormously decreased as compared with its position in dust-free non-energized air. The nuclei are therefore throughout correspondingly larger in size. The nucleation soon rises with an approach to the characteristic slope referred to, showing that the representative ions lie within a relatively narrow range of sizes, the curve of distribution terminating in a maximum. With increasing exhaustion the nucleation first decreases to a minimum; hence to all appearances the ions are now partially destroyed or else materially reduced in size at low pressure, so as to fail of capture even in the higher exhaustions. Beyond the minimum the final and most interesting stage of variation characteristic of weak ionization may be observed. The nucleation rapidly rises again, eventually to approach the asymptote of dust-free air. In explanation of this phenomenon, we may agree that further nuclei are destroyed or rendered relatively inefficient by the low pressure until there is a sufficient excess of supersaturation to actually capture the colloidal nuclei of dust-free air more and more fully in the presence of the ions (few in number and small in size) remaining. Possibly the relative number of ions and colloidal nuclei is itself a sufficient reason; but it since seems clear that an apparatus which ceases to produce condensation on colloidal nuclei much below $\delta p = 35$ cm. can not be expected to regain efficiency between $\delta p = 35$ and $\delta p = 45$ cm., unless there is destruction of whatever has been holding down the effective nucleation to low numbers. As the ions decrease either in size or number, there is a reappearance of the normal colloidal nucleation of dust-free air. Its asymptote is less and less depressed.

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* The coincidence between my interpretation of Wilson's disk colors and my own data holds only when the drop of pressure is observed at the fog chamber. See section 48.

Under *moderate ionization*, such as is obtained from the X-ray bulb at a distance of 1 to 2 meters, the fog limit is definitely reduced, showing the presence of an order of larger nuclei; the asymptotes are correspondingly higher and they are reached later (*i. e.*, at higher exhaustions), indicating the presence of smaller nuclei than in the preceding cases, as well as larger nuclei, unless the increased presence of the latter retards condensation on the former. The range of sizes within which the representative nucleations lie is definitely extended in both directions, but particularly on the sides of the smaller nuclei. The maximum and the minimum are flattened, though destruction of ions still occurs at low pressure.

The new feature of these curves is their failure to rise from the minimum toward the asymptote of dust-free air. It follows that the ions are now present in too large a number, even relatively to their reduced sizes at high exhaustion (if this obtains), to leave an excess of supersaturation sufficient to catch the colloidal air nuclei; or, from the other point of view, the kinetic ionization pressure is too strong to admit of sufficient rupture of the nuclei even at the lowest pressures applied. (Section 43.)

In the comparison of both series of experiments, the occurrence of the intersection of the curve is noteworthy. In other words, the nucleation, apparently produced at high exhaustion by an X-ray bulb at 6 meters from the fog chamber, may be much larger than the nucleation produced from 200, 100, or even 50 cm., due (as we have supposed) to the reappearing efficiency of the colloidal nuclei in the former case. Similar complications surround the distance effects at other pressures; but under conditions of sufficiently moderate exhaustion, *i. e.*, below the fog limit of filtered air, the distance effects between 50 and 600 cm. remains disproportionately small.

When the ionization is relatively *intense*, as when the anticathode is from 10 to 60 cm. from the thinner side of the glass fog chamber, the fog limit has decreased somewhat further, showing increased abundance of the larger nuclei; but the slope closely resembles the corresponding case for dust-free air. There is no maximum, but a terminal asymptote, or better, a terminal corona of fixed aperture. This corona, which is here the largest obtainable in the fog chamber, is even at the highest ionizations reached at supersaturations below the coronal fog limits for dust-free air, and long before the apparatus has ceased to function. It is impossible to state whether colloidal nuclei are simultaneously present but inactive or whether their inefficiency is due to actual absence. It thus becomes a problem of great theoretical importance in its bearing on this subject to determine how the precipitated supersaturation is distributed among groups of nuclei of different sizes.

It is finally to be observed that the terminal corona is the same, both for the ionized and the non-ionized state of the gas. The maximum number of nuclei which can be caught per cubic centimeter seems, therefore, to be a constant for the apparatus and the medium inclosed, and to be independent of the size of the nuclei, whether large like the ions or small like the colloidal nuclei. In the above apparatus, with an air-water medium it is difficult to pass beyond the large green-blue-purple corona.

43. Radiant fields.—The occurrence of a succession of groups of colloidal nuclei of (let us say for simplicity) continuously decreasing size and continuously increasing number, is suggestive; for each group is essential in the given natural but otherwise unknown environment. They are at once restored if withdrawn. These conditions may be imitated or varied artificially by approaching the radium tube at different distances from the fog chamber, in which case the efficient nucleation will for weak radiation usually decrease, as the intervening distances are smaller.

Furthermore, in the presence of radium the character of the phenomenon is the same, except that the nuclei are throughout larger. Withdrawn by precipitation they are at once restored. They are an essential part of air in the new (radiant) environment and the nuclei are again graded.

It is natural to compare the particular nuclear status introduced in the latter case by a particular kind of radiation (gamma-rays) with a former case of dust-free air in the absence of recognized radiation. In other words, if we abstract from the details of the mechanism which are unknown for the colloidal nuclei, chemical agglomeration might be considered referable to some radiant field, unknown but otherwise essentially alike in kind, to the much coarser nucleations observed on exposure to the known radiant field. The effect of radium, however distant, is virtually an increase of size of the efficient air nuclei and a decrease of their number. Hence if we were to fancy that the colloidal nucleation of air responds to its own radiant environment, this would have to be special in kind.

Recently I have made similar tentative inquiries as to whether the ions and persistent nuclei might not be regarded as colloidal nuclei aggregated by kinetic pressure, corpuscular or undulatory; for in view of the occurrence of pronounced secondary action within the fog chamber, the radiation at any point must be considered as sufficiently the same in all directions to be equivalent to a Lesage medium. It is then possible to account for the nucleation in any ionized field, for fleeting and persistent nuclei, for condensational differences of positive and negative ions, for fleeting nuclei otherwise identical but respectively charged and uncharged, for the destructive effect of low pressure and the counteraction in strong ionized fields, for electrical differences in the effect of ultra-violet light and of X-rays, etc., with a single straightforward hypothesis.

While such a view may be worth a statement, it would at the outset encounter very determined opposition; and the distinctive or differentiating evidence to sustain it is uncertain. Briefly, if we admit that with ions sufficiently large and sufficiently numerous, relatively speaking, the colloidal nuclei are virtually non-existent (so far as the fog chamber is concerned), since the former capture all the available moisture, most of the phenomena of nucleation admit of interpretation, and additional hypotheses, however alluring, are not called for. Moreover, so long as the representative colloidal nuclei are definitely smaller than the smaller ions, even in the strongest electrical field—in other words, if what may be called the shattering action of strong fields always fails to reveal ionized nuclei as small as the representative colloidal nuclei—the special interpretation is not warranted.

In conclusion, if we asked what is the most important outcome of researches of the present character, I should refer to the appearances obtained, indicating that a gas, or at least a moist gas, far from being a uniform system, behaves like an assemblage of nuclei which decrease in size and increase in number as the molecular dimension is approached. Every group of nuclei is none the less a structurally essential part of the gas and (be the number of groups few or many) is at once restored if withdrawn, while the molecule itself is distinguished among the many nuclei of its own kind by the maximum frequency of occurrence.

In the above cases (fig. 25) the occurrence of nearly identical slopes for colloidal nuclei and for strong ionization may thus be regarded as the initial branch of a law of distribution of sizes given by the theory of dissociation.

COLLOIDAL NUCLEI IN DUST-FREE AIR. EXHAUSTION PIPES AND STOPCOCKS FOUR INCHES IN DIAMETER.

44. Purpose.—In the above experiments, the efficiency of the fog chamber in regard to the capture of very small nuclei was successively increased by enlarging the efflux pipe in diameter as far as 2 inches. In the present experiments a further step is taken by increasing the diameter to 4 inches. This final step, however, did not show the marked improvement which might have been anticipated, while the difficulty of manipulating a plug weighing 25 pounds is obvious. The limiting coronas here, as above, were the large green-blue-purple type, and in no apparatus of the present kind has it been certainly possible to exceed this in angular aperture. The use of so large a stopcock introduces other difficulties. It is in the first place nearly impossible to make it quite tight. Provision against the influx of *external* air may be made in perfection, by aid of an annular oil bath of the above form; but slow leakage from the fog chamber to the vacuum chamber around the plug could not be avoided. This is an inconvenience, though it need not introduce serious error. With a tightly packed filter the air within the fog chamber is never quite at atmospheric pressure, but a few millimeters below it, so that the exhaustion begins at a lower pressure than 76 cm.

45. Apparatus.—This is shown in fig. 26, where *F* is the fog chamber, *V* the vacuum chamber, *C* the 4-inch stopcock between, *P* the air pump. The pressure within the vacuum chamber is given by the gage *G*, which also communicates with the air pump. The latter may be shut off by the glass two-way stopcock *c*, which serves also for the admission of dust-free atmospheric air when pressure is to be lowered through the filter *f*. The gage *g* is in communication with the fog chamber by the rubber pipe *ab*, which contains a lateral branch (not shown) with a fine screw stopcock through which thoroughly dust-free air may be admitted into the fog chamber from a long well-packed filter (not shown) beyond the cock.

The heavy plug of the stopcock is handled at *h* and counterpoised by the spring *p* on a pulley. By properly adjusting the tension (taking care to allow for excess and diminution of air-pressure), the plug may be rotated as easily and quickly as a much smaller valve. There is no evidence that increased speed in the rotation of the stopcock would have increased the efficiency of the fog chamber. The limit reached depends rather on the law of flow, the gradient of which eventually vanishes. The projecting rims, *m* and *n*, of the stopcock and lower end of the plug, form annular troughs into which oil or mercury may be poured (iron stopcock) and the inflow of the external air absolutely avoided. The cock, moreover, is in this way virtually floated in oil; though no such provision is possible to avoid leakage from *F* to *V* through *C* as already stated.

The goniometer for the measurement of the angular diameter of the coronas is shown somewhat indistinctly at *D*. The small vertical plate which serves as the eye rest is 40 cm. from the axis of the fog chamber, to which it is rigidly attached, but with freedom of rotation about a vertical and horizontal axis and translation along the latter. The arms are 30 cm. long, opened and closed by a tangent screw. The point source of light (not shown, part of a Welsbach mantle) lies 250 cm. behind the fog chamber, in the same horizontal plane.

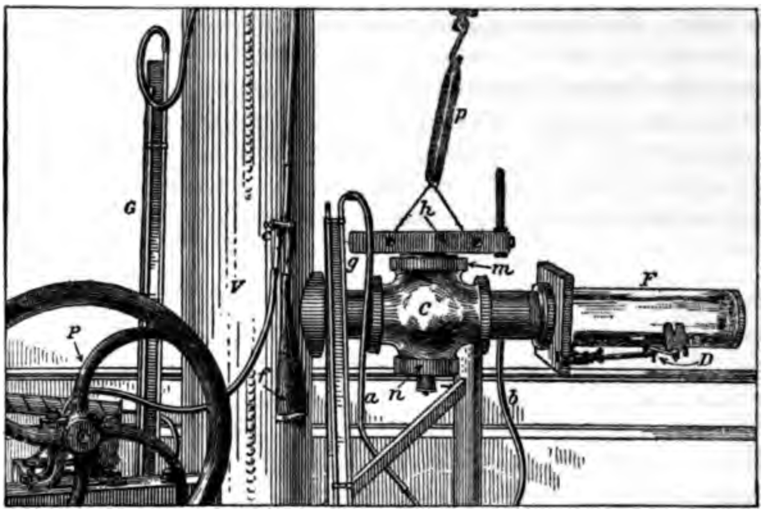

FIG. 26.—Disposition of apparatus in case of fog chamber (*F*) and vacuum chamber (*V*) connected by a 4-inch exhaustion pipe, etc.

The X-ray bulb, adjustably placed with the induction coil and interrupter on a table provided with wheels, could be moved as near to the fog chamber, or remote from it, as desirable, with facility.

The fog chamber itself was a cylindrical jar of glass, provided with a metallic face held in place by bolts and tightened by a rubber gasket. Wax-resin cement was used in liberal quantity everywhere, and internal metallic parts were so far as possible covered with a coat of it. In later experiments a cylinder of wet cloth was placed in the tube between *C* and *F*, to saturate air, in addition to the rectangular framework within the fog chamber.

46. Exhaustion difficulties.—As the stopcock was not tight internally, the final or isothermal pressure in the fog chamber could not be registered. In any case it is doubtful whether the cock can be closed again quickly enough. It was therefore customary in the following experiments to put the vacuum chamber and the fog chamber in contact for a short time, after isothermal conditions had been reestablished. Long communication between the fog chamber and the vacuum chamber is unadvisable from other points of view, since the character of the nucleation of the latter is not so well guaranteed It is therefore necessary to ascertain the conditions under which exhaustion takes place.

Let v be the volume of the fog chamber, V the volume of the vacuum chamber, k/c the ratio of specific heats of the moist gas, and let p, v, τ, ρ, denote its pressure, volume, absolute temperature, and density, under conditions given by the subscripts. It will be convenient to refer to the vacuum chamber by the same symbols with *accents*. Hence the successive thermal states will be for dry air,

For the fog chamber......	Initially................	$p=76$,	τ	ρ
	Adiabatically (alone).....	p_1	τ_1	ρ_1
	Isothermally(alone)......	p_2	$\tau_2=\tau$	$\rho_2=\rho_1$
	Isothermally (together)...	p_3	$\tau_3=\tau$	ρ_3
For the vacuum chamber..	Initially...............	p'	$\tau'=\tau$	ρ'
	Adiabatically (alone)....	$p'_1=p_1$	τ'_1	ρ'_1
	Isothermally (alone)	p'_2	$\tau'_2=\tau$	$\rho'_2=\rho'_1$
	Isothermally (together)..	$p'_3=p_3$	$\tau'_3=\tau_3$	$\rho'_3=\rho_3$

The equations describing the transformations are (again for dry air):

1.......... $$\frac{\tau}{\tau}=\left(\frac{p}{p_1}\right)^{(k-c)/k} \qquad \frac{\tau}{\tau'_1}=\left(\frac{p'}{p_1}\right)^{(k-c)/k}$$

2.............. $$\left\{\begin{array}{ll} p=R\rho\tau & p'=R\rho'\tau \\ p_1=R\rho_1\tau_1 & p'_1=R\rho'_1\tau \\ p_2=R\rho_2\tau=R\rho_1\tau & p'_2=R\rho'_2\tau=R\rho'_1\tau \\ p_3=R\rho_3\tau & \text{or } p_2/p'_2=\rho_2/\rho'_2 \end{array}\right.$$

3................ $$\rho v+\rho^1 V=\rho_1 v+\rho'_1 V=\rho_2 v+\rho'_2 V=\rho_3\,(v+V)$$

From these one may deduce, relative to the value of p_1,

$$v\,(p^{(k-c)/k}p_1^{c/k}-p_3)=V\,(p_3-p'^{(k-c)/k}p_1^{c/k})$$

or

4................. $$p_1^{c/k}=\frac{p_3\,(1+v/V)}{p'^{(k-c)/k}+(v/V)\,p^{(k-c)/k}}$$

5.................. $$p'_2+p_2\cdot v/V=p_3\,(1+v/V)$$

where p, p', p_3, are observable with certainty. While equation (5) is variously useful in checking the results, it does not admit of the individual determination of p_2 and p'_2. For this purpose, however, the equations (1) and the second and third of group (2) are available, with the results (for dry air)

$$6 \ldots\ldots\ldots\ldots p_2 = p^{(k-c)/k} p_1^{c/k} \qquad p'_2 = p'^{(k-c)/k} p_1^{c/k}$$

since $p_1^{c/k}$ is given in equation (4).

Using these equations, the data of table 17 were computed, in connection with incidental results tested for the purpose.

TABLE 17.—Values of adiabatic (p_1) and isothermal (p_2, p'_2) pressure for dry air. Pressures computed from the initial pressures ($p = 76$, p') and the final common isothermal pressure p_3 of the communicating fog and vacuum chambers with other similar data. Volume ratio $v/V = 0.064$; temperature 20°.

Observed.				Computed.*			Observed. $\tau_1 - t_1 = 273$ $\tau'_1 - t_2 = 273$		
p.	p'.	p_3.	†p'_1.	p_1.	p_2.	p'_2.	‡p''_1.	t_1.	t'_1.
76	43.0	45.4	48.0	45.7	....	....	....	....	....
	39.5	42.2	45.2	....	....	....	....	....	....
	42.5	45.2	47.9	....	....	....	....	....	....
	43.5	45.5	47.9	45.7	52.9	45.0	45.6	−20.2°	24.3°
	45.5	47.3	49.3	....	....	....	47.4	....	....
	47.5	48.9	50.9	....	....	....	48.9	....	....
	51.5	52.5	54.3	52.4	58.3	52.1	....	− 9.9°	21.5°
	53.5	54.3	56.1	....	....	....	....	....	....
	55.5	—	—	....	....	....	....	....	....
	57.5	58.0	59.8	....	....	....	....	....	....
	59.5	59.7	62.2	59.4	63.8	59.4	—	.2°	20°
	43.5	45.7	48.4	....	....	....	....	....	....
	43.5	45.4	48.0	....	....	....	....	....	....

* Checked $p'_2 + p_2 v/V = p_3 (1 + v/V)$.

† Observed as soon as possible at the fog chamber. Nearly same later.

‡ Observed as soon as possible at the vacuum chamber. $p''_1 = p_3$ nearly.

The data of table 17 are computed for dry air throughout and are given in fig. 27*a*, graphically.* The results of the table are very important. In the first place, it will be seen not only that isothermal pressures or nearly isothermal pressures are not observed, but that the effect of the vacuum chamber is preponderating. Thus the pressure at the latter (p''_1) read off as soon as possible and nominally adiabatic is within 1 mm. of p_3. Similarly the computed adiabatic pressure (p_1) is within a few millimeters of p''_1 and p_3. It follows, therefore, that even an approach to isothermal pressure can not be discerned at the fog chamber at all, to say nothing of adiabatic pressure; or that before the exhaust cock can be closed again, the vacuum chamber has practically regained its isothermal pressure by cooling and that the fog chamber is further exhausted by a corresponding amount. The pressure $p'_1 = p''_2$ observed under isothermal conditions[*] at the fog chamber exceeds p_1 (computed) by about 1.9 cm. on the average, which might be regarded as the average vapor pressure of water at the temperature at which the observation was made. Leaving this for further consideration, the final result of importance is the following: p_2, the computed isothermal pressure in the closed fog chamber, is from 2 to 5 cm. above the observed (nominally) isothermal pressure $p'_1 = p_2$ (observed), and correspondingly more than this above the common isothermal value (p_3) usually taken. For the region in which colloidal nuclei lie the correction will be in excess of the difference between the pressure regions containing Wilson's data for colloidal nuclei, as reduced elsewhere,[†] and the region in which my own data as summarized below would lie. In other words, the data in my large coronal apparatus lie in regions of exhaustion at least as moderate as those observed in Wilson's small apparatus; or the two types of apparatus compare in efficiency if the drop of pressure taken is not the apparent experimental value but that deduced for the computed isothermal pressure (p_2) of the fog chamber, as above explained.

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*The curve (p_2) is of no interest here and should be disregarded.

47. The same, continued. Case of air in the fog chamber saturated with water vapor.—It will next be necessary to compute the above data with allowance for the vapor pressure of water in the fog chamber, supposing the vacuum chamber to be dry, which may seem to be in a measure true, since it is heated by the same transfer of air which cools the fog chamber. Hence in the summary, if π is the vapor pressure of water, the equations relating to the fog chamber have to be modified to

$$1 \ldots\ldots\ldots\ldots\ldots\ldots \frac{\tau}{\tau_1} = \left(\frac{p - \pi}{p_1 - \pi_1}\right)^{(k-c)/k}$$

$$2 \ldots \begin{cases} p - \pi = R\rho\tau \\ p_1 - \pi_1 = R\rho_1\tau_1 \\ p_2 - \pi = R\rho_2\tau = R\rho_1\tau \\ p_3 - \pi = R\rho_3\tau \qquad p_3 = p'_3 = R\rho'_3\tau_3 \qquad \rho v + \rho^1 V = \text{etc.} = \rho_3 v + \rho'_3 V \end{cases}$$

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[*] This pressure varies but slightly.

[†] Presidential address, Physical Review, XXII, 1906, p. 107.

From these the value of p_1 appears as

$$7 \ldots\ldots\ldots p_1^{c/k} = \frac{p_3 + (p_3 - \pi) \cdot v/V}{p'^{(k-c)/k} + (p-\pi)^{(k-c)/k}(1 - \pi_1/p_1)^{c/k} \cdot v/V}$$

where π_1/p_1 occurring with the factor v/V may be neglected. Furthermore

$$8 \ldots\ldots\ldots (p_2 - \pi) = (p - \pi)^{(k-c)/k}(p_1 - \pi_1)^{c/k};\ p'_2 = p^{1\,(k-c)/k}\, p_1^{c/k}$$

where π_1 (respectively π =0.10, 0.24, 0.51 in comparison with p_1=45.6, 52.2, 59.3) may again be neglected.

The results of this computation are given in table 18 and fig. 27*b*. Table 18 also contains the value of δp observed as $p-p_3$ and computed as $p-p_2$, the latter being the correct value. This table of corrections will not apply below the limits of computation, since π_1 now becomes appreciable in comparison with p_1; but above $p-p_3$ = 15 cm., a table may be constructed from which $\delta p = p-p_2$ may be taken at once. In this way the following data will be corrected. Since the main data for colloidal nuclei lie between $p-p_3$ = 25 cm. and 32 cm., the correction will lie between –4 cm. and –6 cm.

TABLE 18, corresponding to table 17 for saturated moist air in the fog chamber. Temperature 20°; vapor pressure 1.7 cm.; p = 76; v/V = 0.064.

δp.		Observed.				Computed.				
$p-p_3$.	$p-p_2$.	p_1.	p_3.	*p_1'.	†p_1''.	p_1.	p_2.	p_2'.	τ_1.	τ_1.
30.5	25.2	43.5	45.5	47.9	45.6	45.6	50.8	44.9	−18.7	+24.0
23.5	19.9	51.5	52.5	54.3	....	52.2	56.1	52.0	− 8.5	21.2
16.3	14.4	59.5	59.7	62.2	....	59.3	61.6	59.3	+ 1.5	+20

* Observed as soon as possible at the fog chamber; nearly same later.
† Observed as soon as possible at the vacuum chamber; $p_1'' = p_3$ nearly.

TABLE 19.—The results are for π = 1.7 at 20°.

p.	p^1.	p_3.	p_2.		
			v/V = 1.	v/V = 0.064.	v/V = 0.
76−π	43.5	45.5	48.1	50.8	53.1
	51.5	52.5	54.4	56.1	58.4
	59.5	59.7	60.7	61.6	63.7

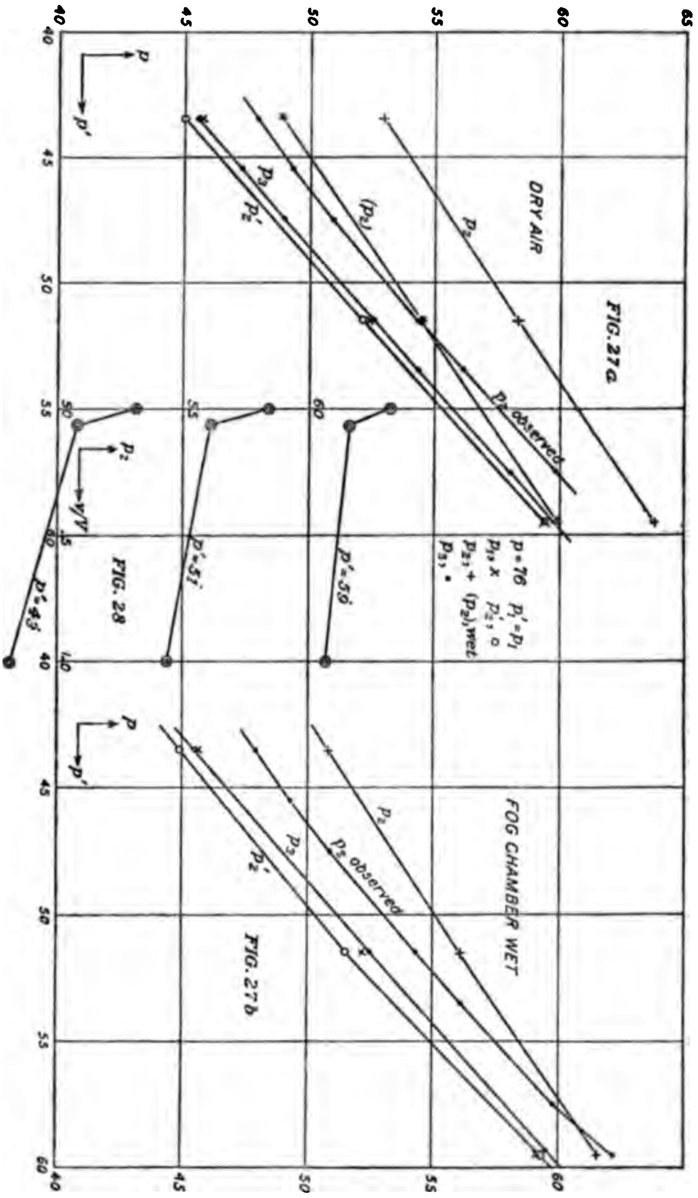


Fig. 27*a*.—Computed pressures in the fog chamber and in the exhaustion chamber for atmospheric pressure, p in the former and p' in the latter. Dry air. Table 17.

Fig. 27*b*.—Wet air in the fog chamber. Table 18.

Fig. 28.—Isothermal pressure in the isolated fog chamber for different volume ratios (v/V) of the fog chamber and vacuum chamber. Table 19.

It may be of further interest to compute the values of $p-p_3$ for $v/V=1$ (a small exhaustion chamber) and for $v/V=0$ (one of immense size) for the same values of p, p', p_3, observed isothermally and initially at the fog chambers and vacuum chambers and finally when both are in communication. The results for 20° are given in table 19, page 56.

These data are charted in figs. 28 and 30, to a first approximation, in terms of v/V and p_3. If expressed in terms of p', they lie nearly on straight lines, as do the above values of p_2 for $v/V=0.064$. The large

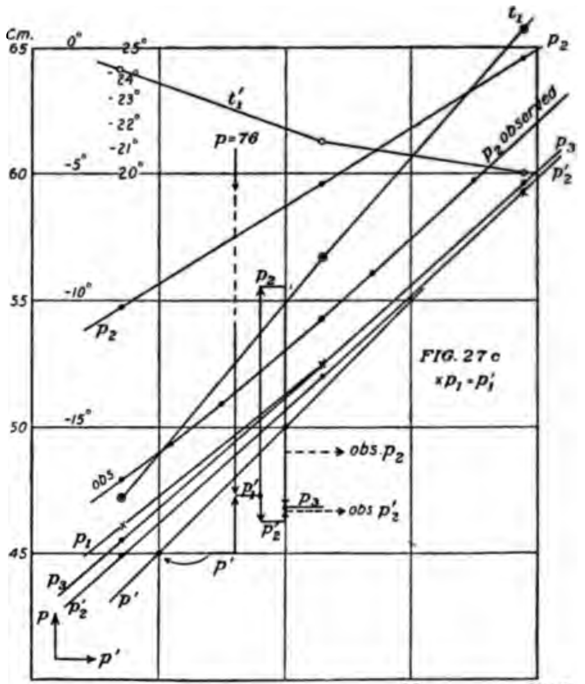


FIG. 27c.—Wet air in both chambers. Table 20.

variation between $v/V=0$ and 0.064 as compared with the small one for $v/V=0.064$ and 1.0 is noteworthy. Hence, in using small vacuum chambers, the observed and computed p_3 and p_2 lie more closely together, but other disadvantages supervene. The rate of variation

$$\frac{\delta p_2}{\delta(v/V)}=p_3(p/p')^{(k-c)/k}\frac{1-(p/p')^{(k-c)/k}}{\left\{1-(p/p')^{(k-c)/k}.v/V\right\}^2}$$

is always negative and proportional to p_3 and $(p/p')^{(k-c)/k}$.

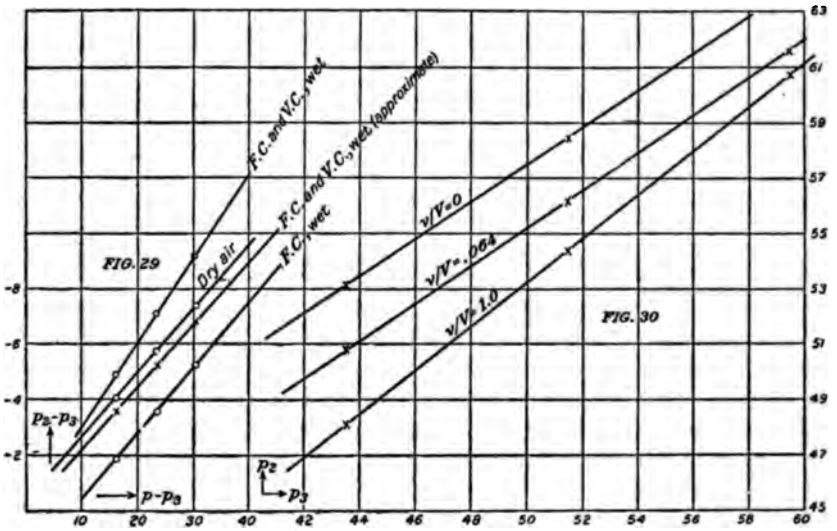


FIG. 29.—Corrections ($p_2 - p_3$) for $\partial p = p - p_3$. Table 20.

FIG. 30.—Isothermal pressure p_2 in the isolated fog chamber for different isothermal pressures p_3 of the communicating fog chambers and for different volume ratios (v/V). Table 19.

48. Case of saturated air in both chambers.—Here all the pressures of both chambers must be reduced by the corresponding pressure of saturated vapor, except p'_1 where the vapor is slightly superheated. Omitting this the equations become

$$9 \ldots\ldots\ldots (p_1 - \pi_1)^{c/k} = \frac{(p_3 - \pi)\ (1 + v/V)}{(p' - \pi)^{(k\text{-}c)/k} + (p - \pi^{(k\text{-}c)/k} . v/V}$$

$$10 \ldots\ldots\ldots\ldots\ldots (p_2 - \pi) = (p - \pi)^{(k\text{-}c)/k} (p_1 - \pi_1)^{c/k}$$

or the equations again take the original form, though a special computation is needed, since a different initial pressure (p) enters. These results are given in table 20 and in fig. 29.

TABLE 20.—Corresponding to table 18 when both fog chamber and vacuum chamber are saturated. $v/V = 0.064$; temperature 20°; $p = 76$ cm.; $\pi = 1.7$

∂p.	Observed.				Computed.				
$p - p_3$.	$p - p_2$.	p'.	p_3.	*p'_1.	$p_1\pi_1$.	†p_2.	p'_2.	τ_1.	τ_2.
30.5	23.7	43.5	45.5	47.9	43.5	52.4	45.1	−22.5	..
23.5	18.2	51.5	52.5	54.3	50.3	57.8	52.2	−11.5	..
16.3	12.7	59.5	59.7	62.2	57.3	63.3	59.5	− 1.4	..

* Observed as soon as possible at the fog chamber.

† $(p'_2 - \pi) + \frac{v}{V}(p_2 - \pi) = \left(1 + \frac{v}{V}\right)(p_3 - \pi)$

$p-p_3$.	$p-p_2$.	Ratio.	
0	0		
16.3	12.7	$\frac{18.2}{23.5} = 0.7745$	Mean 0.776
23.5	18.2	"	
30.5	23.7	$\frac{11.0}{14.2} = 0.7782$	

$p-p_3$.	Correction.	Ratio.	
0	0		
16.3	3.6	$-\frac{5.3}{23.5} = 0.226$	Mean 0.225
23.5	5.3		
30.5	6.8	$-\frac{3.2}{14.2} = 0.225$	

In view of the low temperature (τ_1) the vapor pressure (π_1) may be neglected for the fog chamber; but this would not be the case of the vacuum chamber, where π'_1 is quite appreciable. As the result of this, the march of pressures in the vacuum chamber is peculiar, but need not be considered here, where p, p', p_3, and p_2 are chiefly in question. The difference between $\delta p_0 = p - p_3$ as observed and $\delta p_c = p - p_2$ as computed now actually vanishes with the former (see fig. 29). In other words, very nearly

$$\frac{p - p_2}{p - p_3} = 0.775, \text{ or } \frac{p_2 - p_3}{p - p_3} = 0.225$$

and therefore $\delta p_0 - \delta p_c = 0.225\ \delta p_0$, nearly. Hence this is a correction to be taken by preference. A table giving $0.225\ \delta p_0$ for the usual ranges of observation was therefore drawn up and used throughout the following work, or the factor 0.775 may be used at once. These corrections are quite sufficient to indicate that the efficiency of the fog chamber as used above is not surpassed by any apparatus.

The preceding correction, in comparison with the cases of sections 46 and 47, seemed to me to be most nearly in keeping with the actual state of the case. The more nearly rigorous solution, when the air in both chambers is continually saturated, leads to transcendental equations for the adiabatic pressures ($p_1 = p'_1$), which can only be obtained approximately. If the vapor pressures (π_1 and π'_1) correspond to p_1 and p'_1, the results would be

$$(p_1 - \pi'_1)^{c/k} = \frac{(p_3 - \pi)\ (1 + v/V)}{(p' - \pi)^{(k-c)/k} + v/V\,.\Big(1 - (\pi_1 - \pi'_1)/(p_1 - \pi'_1)\Big)^{c/k}(p - \pi)^{(k-c)/k}}$$

$$(p_1 - \pi_1)^{c/k} = \frac{(p_3 - \pi)\ (1 + v/V)}{\Big(1 - (\pi'_1 - \pi_1)/(p_1 - \pi_1)\Big)^{c/k}(p' - \pi)^{(k-c)/k} + v/V\,.(p - \pi)^{(k-c)/k}}$$

where approximate values must be entered for π'_1, π_1, p_1, in the denominator on the right side of the equation.

Similarly

$$p_2 - \pi = (p_1 - \pi_1)^{c/k}(p - \pi)^{(k-c)/k},$$

$$p'_2 - \pi = (p'_1 - \pi'_1)^{c/k}(p' - \pi)^{(k-c)/k},$$

$$\tau/\tau_1 = \Big((p - \pi)/(p_1 - \pi_1)\Big)^{(k-c)/k}, \quad \tau/\tau_1' = \Big((p' - \pi)/(p_1' - \pi_1')\Big)^{(k-c)/k}$$

Making use of the values of table 18, the data of table 21*b* were computed on a single approximation.

Table 21*b*.—Corresponding to table 18, when both fog chamber and vacuum chamber are saturated. $v/V = 0.064$; temperature 20°; $\pi = 1.7$; $p = 76$ cm.

$^*\pi$.	$^*\pi'_1$.	obs. p'.	obs. p_3.	p_1.	p_2.	p'_2.	t_1.	t'_1.
0.0	2.3	43.5	45.5	46.1	54.7	44.9	−17.8°	+24.1°
.2	1.9	51.5	52.5	52.5	59.6	52.0	− 8.3	21.3
.5	1.7	59.5	59.7	59.3	64.6	59.4	+ .8	19.8

*Assumed from data for t_1, t'_1, in table 18.

$p - p_3$.	$p - p_2$.	$(p - p_2)/(p - p_3)$.	$\bar{\pi}$.	$\bar{\pi}'_1$.	$\bar{t}_1$.	$\bar{\rho}_1/\rho_1$.	$\bar{p}_2$.
0.0	0.0						
16.3	11.4	$\frac{16.4}{23.5} = 0.70$	0.7	2.2	+ 5.2	0.910	49.9
23.5	16.4		.9	1.9	+ 9.4	.929	55.5
30.5	21.3	$\frac{9.9}{14.2} = .69$	1.1	1.7	+12.7	.952	61.5

The corrections (see table 21*b*, and upper graphs in fig. 30) again lie on a curve which passes through zero, but with a larger slope. In fact, they are so much larger than the preceding cases and throw the whole phenomenon into so low a region of pressures that it has seemed best to abide by the data at the beginning of this paragraph, at least for the present. Details are given in table 21*b*.

A few incidental results deserve brief attention. The first of these is the nearly constant difference of about $\delta p_2 = 2$ cm. between the observed value of p_2 (nominal) and p_3. Since for dry air or not

$$(p'_2 - \pi) + v/V.\ (p_2 - \pi) = (p_3 - \pi)(1 + v/V)$$

is constant for a given exhaustion,

$$\delta p'_2 = -v/V.\ \delta p_2.$$

Hence if $\delta p_2 = 2$ cm.

$$\delta p'_2 = 0.064 \times 2 = 0.13 \text{ cm.}$$

The case is illustrated graphically for $p'=45$ cm. in the notched curves of fig. 27*c* in a way easily understood. It seems probable that whereas the smaller fog chamber has more than returned to isothermal conditions (p_3), the large vacuum chamber is about a millimeter short of it when the cock is again closed. The constancy of this difference is in all probability referable to the systematic method of investigation, though the effect of precipitated moisture has not yet been considered.

Anomalous relations in the data for the fog chamber (as in the case of $p'=59.5$ cm.) are direct errors of observation. On the other hand, however, since within the ranges of observation and very nearly

$$p = a$$
$$p_2 = a_2 + b_2 p'$$
$$p_3 = a_3 + b_3 p'$$
$$(p-p_2)/(p-p_3) = (A_3+B_3p')/(A_2+B_2p') = A + Bp' \text{ (nearly)},$$

where a, b, A, B, etc., are constant. Frequently B is negligible, so that

$$(p-p_2)/(p-p_3) = A = \text{const.},$$

in which case the graph for $(p_2-p_3)/(p-p_3) = 1-A$ also passes through the origin as in the two cases (fig. 30). There is no need of this and it is at best an approximation which facilitates computing.

Some remarks may here find place on the moisture precipitated in the fog chamber per cubic centimeter, and on the absolute temperature $\bar{\tau}_1$ to which this precipitation heats the chamber above the adiabatic temperature τ_1. I have shown above that the combination of fog chamber with a large vacuum chamber and a sufficiently wide passageway, though affording superior practical advantages, and little if any inferiority in efficiency to the piston apparatus within the range of measurable coronas, nevertheless does not give the volume expansion of the air within the fog chamber either under adiabatic or under isothermal conditions. It makes no difference how rapidly the stopcock is manually closed. The conditions of the vacuum chamber are always impressed upon the fog chamber. The adiabatic and isothermal data may, however, be computed if the volume ratio of the fog and vacuum chambers and the pressures before exhaustion (when the chambers are isothermally separated) and after exhaustion (when the chambers are isothermally in communication) are known; and these computations are simple because the reductions are practically linear.

When the vacuum chamber is large, moreover, its pressures vary but slightly, and therefore the pressure observed at the vacuum chamber after exhaustion, when the two chambers are in communication, is very nearly the adiabatic pressure of the fog chamber. This result makes it easier to compute the water precipitated per cubic centimeter (without stopping to compute the other pressures) with a degree of accuracy more than sufficient when the other measurements depend on the size of coronas.

To prove this, let d, L, and π refer to the density, latent heat of evaporization, and pressure of water (or other) vapor; let ρ, k, c, t, denote the density, specific heat at constant pressure, specific heat at constant volume and temperature of the air, the water vapor contained being disregarded apart from the occurrence of condensation. Let the variables, if primed, refer to the vacuum chamber, otherwise to the fog chamber. When used without subscripts, let them refer to isothermal conditions or to room temperature. Let the subscript $_1$ refer to the adiabatic conditions on exhaustion; the subscript $_2$ to isothermal conditions, if the chambers could be isolated immediately after exhaustion and allowed to heat and cool from the adiabatic state independently. This case is in fact realized in the piston apparatus. Let the subscript $_3$, finally, refer to the isothermal conditions which prevail if the chambers are put in communication at a room temperature after exhaustion. Then the usual equations for heat evolved in the condensation of vapor lead easily to

$$\bar{d}=[d_1]-\rho_2 C(\bar{t}-t_1)/L \qquad (1)$$

where $\bar{d}$ is the density of saturated vapor at $\bar{t}$, where $\bar{t}$ is the temperature to which the wet air is heated from its adiabatic temperature t_1, in consequence of the condensation of water vapor, where $[d_1]$ is the density of water vapor if cooled as a gas, *i. e.*, without condensation, from t to t_1. Moreover

$$[d_1]-\bar{d}=m \qquad (2)$$

the mass of water precipitated per cubic centimeter by condensation or the quantities sought.

If Boyle's law is assumed to hold both for the gaseous water vapor $[d_1]$, and for the wet air, it is convenient to reduce equation (1) to room temperature (isothermal state) and it becomes

$$\bar{d}=d\frac{p_2-\pi}{p-\pi} \quad \rho\frac{c}{L}\frac{p_2-\pi}{p-\pi}(\bar{t}-t_1) \qquad (3)$$

If the vapor density of saturated water vapor is known at a temperature as low as $\bar{t}$,

$$\bar{d}=f(\bar{t}) \qquad (4)$$

so that $\bar{t}$, the only unknown quantity in equation (3), since the equation of adiabatic expansion determines t_1, is found from the intersection of the curves (3) and (4). This is the method of Wilson and of Thomson.

In the piston apparatus p_2 as well as p may be read off by the gages; but, as stated above, this is not true when the fog chamber communicates directly with the vacuum chamber. In this case, however, p_1 is nearly given by p_3. Consequently it is expedient to reduce equation (1) to the adiabatic conditions, whence (if τ refers to absolute temperature),

$$d=d\ \left(\frac{p_1-\pi_1}{p-\pi}\right)^{c/k}-\frac{\rho c}{L}\left(\frac{p_1-\pi_1}{p-\pi}\right)^{c/k}(\overline{t}-t_1) \qquad (5)$$

$$\tau_1=\tau\ \left(\frac{p_1-\pi_1}{p-\pi}\right)^{(k-c)/k} \qquad (6)$$

$$m=\frac{\rho c}{L}\left(\frac{p_1-\pi_1}{p-\pi}\right)^{c/k}(\overline{t}-t_1) \qquad (7)$$

Here π_1, the vapor pressure at t_1, is usually negligible (about 0.5) as compared with p_1, and p_1 may, in practice, where great accuracy is not demanded, be replaced by p_3, which, like p, is read off while π holds at t, which is also read off.

In illustration I will give a numerical example taken from table 21*b* where

$p = 76$ cm.
$\pi = 1.7$ cm.
$\rho = 0.00118$
$p' = 43.5$ cm.

$p_3 = 45.5$ cm.
$p_1 = 46.1$ cm.
$p_2 = 54.7$ cm.

$t_1 = -17.8°$ C.
$\overline{t} = 5.25°$ C.
$t'_1 = 24.1°$ C.

If equation (3) is taken

$$m=5.36\times10^{-6} \text{ grams per cubic centimeter}$$

If equation (5) is taken

$$m=5.35\times10^{-6}$$

If equation (5) is taken and p_1 replaced by p_3

$$m=5.30\times10^{-6}$$

the error being 1 per cent of the true value, which is quite near enough in practice and admits of easy correction.

Finally one may compute $\overline{p}_2$, the pressure which would be observed at the fog chamber instead of p_2 if allowance is made for the water precipitated in the fog chamber, whereby additional air escapes into the vacuum chamber, since the former is heated from τ_1 to $\overline{\tau}_1$. The chambers are supposed to be separated (cock closed) immediately after condensation and no further loss of air is to take place from fog chamber to vacuum chamber while the absolute temperature of the fog chamber passes from $\overline{\tau}_1$ to atmospheric τ. Without giving the full discussion for which there is no room, I will merely add that

$$p_2-\pi=\frac{\overline{\rho}_1}{\rho_1}(p_2-\pi)$$

where $\overline{\rho}_1$ is the density of the air at $\overline{\tau}_1$. The ratio is equal to

$$\frac{\overline{\rho}_1}{\rho_1}=\frac{(\overline{\pi}'_1-\overline{\pi}_1)-(\pi'_1-\pi_1)+(p_1-\pi_1)\,(1-v/V\cdot\tau'_1/\tau_1)}{(p_1-\pi_1)\,(\overline{\tau}_1/\tau_1+v/V\cdot\tau'_1/\tau_1)}$$

if the vapor pressures π are designated like the temperatures and pressures with which they are associated. Usually

$$\frac{\overline{\rho}_1}{\rho_1}=\frac{1+v/V\cdot\tau'_1/\tau_1}{\overline{\tau}_1/\tau_1+v/V\cdot\tau'_1/\tau_1}$$

suffices, the term involving the vapor pressures (π) being a correction of about 1 per cent. The computation, to which I shall return elsewhere, shows that $\overline{p}_2$, computed, is always above $\overline{p}_2$, observed, so that the fog chamber begins to heat itself above the temperature $\overline{\tau}_1$ before the cock can be closed again and contains less than its normal allotment of air. Thus, in the example given, $\overline{\rho}_1/\rho_1=0.91$; $\overline{p}_2=47.9$, observed; and $\overline{p}_2=49.9$, computed. Hence p and p_2 alone have any definite meaning for the fog chamber.

49. Observations with 4-inch exhaust pipes.—The observations of this paragraph, apart from the exhaustion difficulties already discussed, were made peculiarly difficult by the unavoidable leak from fog chamber to vacuum chamber through the large exhaust cock. It was therefore essential to wait many hours for each observation, since the coronas corresponding to the second, third, etc., of successive exhaustions were smaller than the first. This can not be due to any other cause than the presence of water nuclei from the fog of the first exhaustion. A given corona, moreover, was apt to decrease in aperture as much as one-half during the period of subsidence, showing growth of certain particles at the expense of others, the latter being afterwards detected in the water nuclei specified. This must also be attributed to the continued slow exhaustion due to the leak in question.

In table 21 and fig. 31 the earlier data with 4-inch pipes are given, chiefly with the object of direct comparison with foregoing results with 2-inch pipes. The meaning of the data is clear from the earlier tables, and the δp here mentioned is the isothermal value observed at the fog chamber as heretofore.

On March 16 to 18 the data are irregular in the way common to observations in a newly adjusted apparatus. The effective nucleation is too small from the presence of interior sources of relatively bulky nuclei. A fairly complete series was undertaken on March 19. The outgoing and incoming branches do not quite coincide, and the data, as a whole, still lie below the corresponding results with 2-inch exhaustion pipes. This is indicated in fig. 31. Of later observations (March 22),

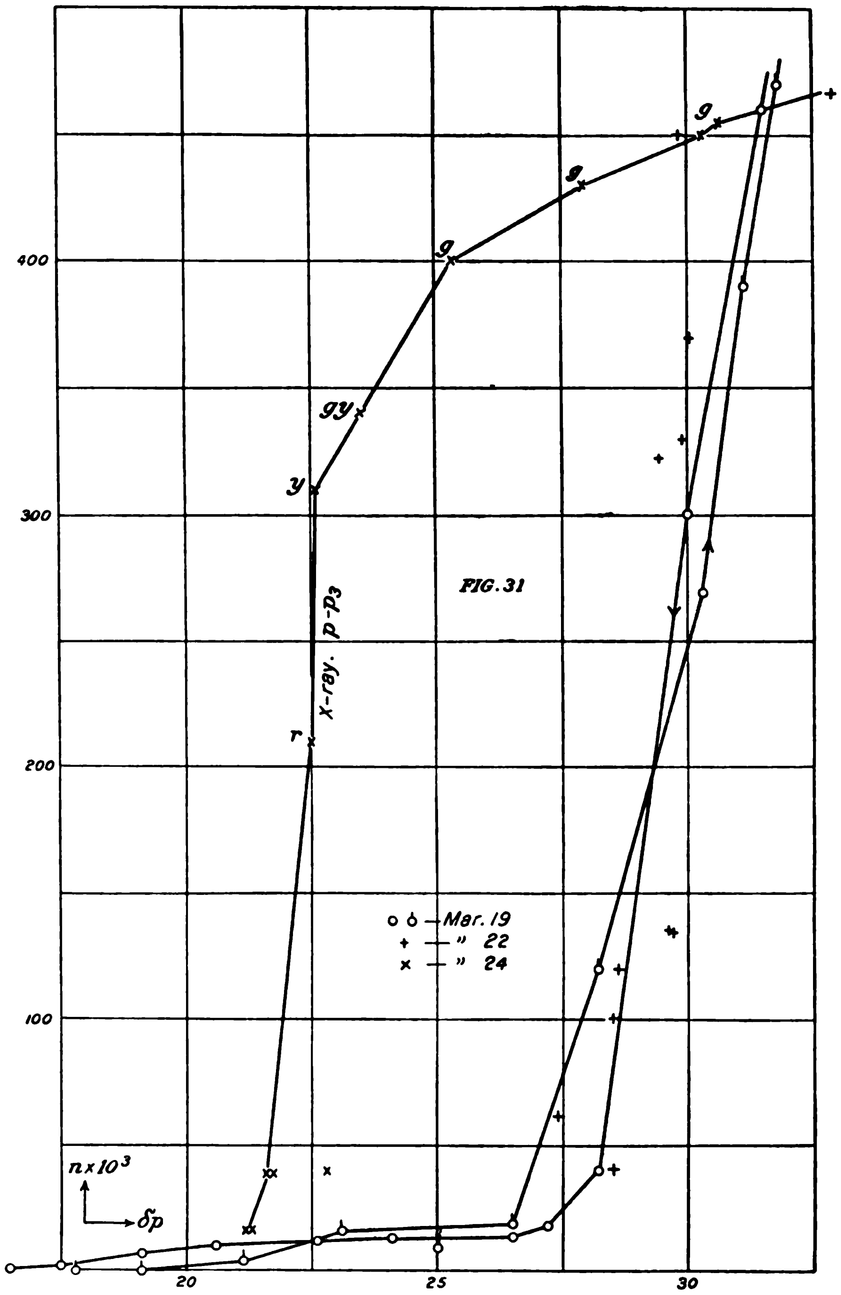


FIG. 31.—Nucleations (n) observed in dust-free air and dust-free X-air at different exhaustions (δp); 4-inch pipes. Table 21.

TABLE 21.—Colloidal nuclei in air. New apparatus. Glass fog chamber. Piping 12 inches long, 4 inches in diameter; 4-inch plug stopcock.

	Observed δp.	s.	Cor.	$n \times 10^{-3}$.
I. Mar. 16	25.4	3.8	.....	20
Later...	25.4	2.0	.....	3
	25.4	[1]3.8	.....	20
	29.0	3.5	.....	[2]16
	29.0	4.2	.....	27
II. Mar. 17	20.4	.0	.....	0
	25.1	3.3	.....	12
	25.1	4.2	.....	25
	29.1	5.1	.....	51
	29.1	3.7	.....	20
	29.1	4.2	.....	28
	33.5	[3]7.3	w y′	140
	33.5	11	w y	315
	33.5	11	w y	315
	38.0	[3]7.2	w B P	165
	38.0	11	w y′	330
	42	10	w o	350
	42	11	w y	350
Later...	33.5	12.0	g y o	425
	33.5	4.2	cor	30
	33.5	[2]9.5	w o	315
III. Mar. 18	33.5	11.5	g y o	425
	....	8.8	w p cor	190
	....	9.8	w o	315
	....	[2]4.6	cor	41
	....	[2]11.8	y′ o b g	390
IV. Mar. 19	33.5	[2]13	Stone-blue	
	33.5	7.0	w y	
	33.5	12.0	g y o	
	46.4	[4]13	g B P	540
Incoming series.	42.2	13	b′ B	510
	38.0	13	g B P	500
	33.4	....	g y o to g B	[4]425
	31.5	....	g B P	460
	30.0	11	w o g	300
	28.2	4.7	cor	40
	27.2	3.6	cor	18
	26.5	3.4	cor	14
	24.1	3.4	cor	13
	22.6	3.4	cor	12
	20.6	3.3	cor	10
	19.1	2.9	cor	7
	17.5	1.9	cor	2
Incoming series.	16.5	....	Rain	1
	15.1	....	Rain	1
Later...	16.5	....	Just seen	1
Outgoing series after several hours' rest.	17.8	0	No corona	0
	19.1	0	No corona	0
	21.1	2.2	cor	3
	23.1	3.6	cor	16
	25.0	3.1	cor	9
	26.5	3.7	cor	19
	28.2	7.1	w y g	120
	30.3	9.7	w o g′	270
	32.1	11	w y b g	390
	32.8	12	g B P	470
Promiscuous results.				
V. Mar. 20	[5]29.8	....	g B P	450
Later...	30.0	....	y o b g	370
	30.3	....	g B P	450
	28.0	....	g y o	390
	27.3	11	w r′ g	250
	26.2	....	w p cor	165
VII. Mar. 22	28.6	[6]6.9	g B P	120
	26.3	4.5	cor	33
	27.4	5.5	cor	62
	29.9	10	y o b g	330
	33.9	11	g B P	475
Later...	33.8	11	g B P	475
	32.7	....	g y o	420
X. X-rays; $D = 20$ cm.	33.6	11	g B P	470
	30.6	11	g B P	455
	27.9	11	g B P	430
	25.3	11	g B P	400
	21.7	5	cor	39
	21.6	5.0	cor	39
	22.5	10.5	w r g′	210
	23.5	....	g y o	340
	22.8	5.0	cor	40
	22.6	10	w y g	310
	21.5	3.6	cor	16
	21.6	3.7	cor	17

[1] $s = 3.8$ persistently except on first exhaustion.

[2] Many periods follow.

[3] Blurred; other coronas very clear, often multi-annular.

[4] Periods usually omitted.

[5] Fog chamber greasy.

[6] Followed in next exhaustion by small corona.

[7] Apparatus cleaned again.

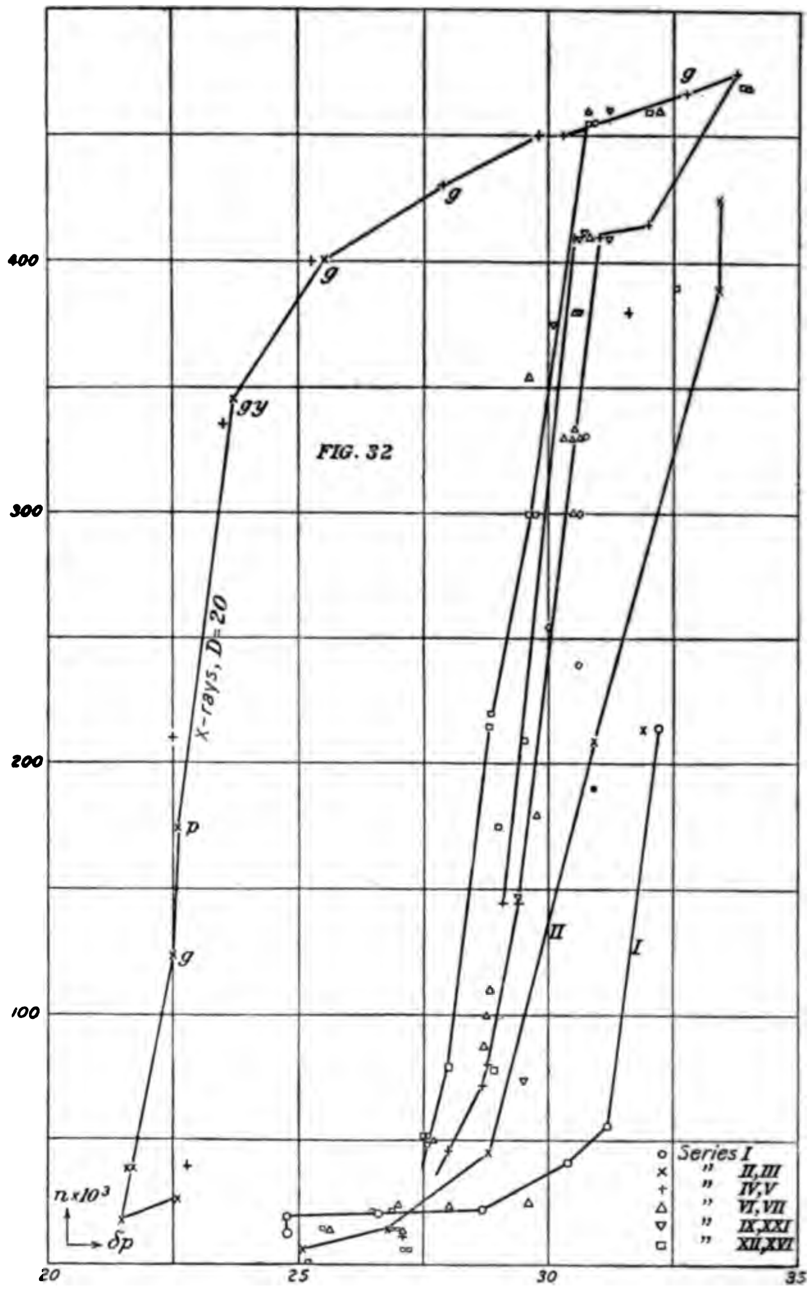


FIG. 32.—Nucleations (n) observed in dust-free air and dust-free X-air at different exhaustions (δp); 4-inch pipes. Table 23.

TABLE 22.—Systematic work. Third cleaning of apparatus. Isothermal $\delta p = p - p_s$; $p = 76$ cm.

	δp.	s.	Cor.	$n \times 10^{-3}$.
I. Mar. 26	24.8	3.4	cor	13
	24.8	3.8	....	20
	24.8	3.9	....	20
	26.6	3.9	cor	21
	28.7	4.0	....	23
	30.4	4.7	....	42
	31.2	5.2	w b r	56
	32.2	8.6	w p	215
II. Later...	33.4	13	g y o	425
	33.4	9.5	w p cor	240
	33.4	11.5	w y b g	390
	33.4	9.5	w b r	250
	30.4	8.7	w p cor	210
	28.8	5.0	cor	46
	26.8	3.5	cor	15
	25.1	2.7	cor	7
	22.0	2.1	Faint cor	2
III. X-rays from $D = 20$ cm.	21.5	3.8	cor	18
	23.7	11	Vague g y o	345
	22.6	4.4	cor	27
	22.5	6.7	Vague g B P	124
	22.6	8.7	w p cor	175
	25.5	....	g Fog	400
IV. Mar 27, 2d day.	[1]30.5	....	g y o	410
	31.6	10	yo bg	380
	29.1	10	w o g	145
V. Later...	31.0	12	g y o	410
	30.4	4.8	cor	45
	29.4	7.4	wp	145
	28.7	5.8	cor	72
	28.0	5.0	cor	46
	27.1	3.3	....	12
	28.0	4.2	....	27
	28.8	6.0	w y	80
	30.0	7.2	w B P	150
	30.6	8.1	wP cor	180
	31.4	7.0	w y	130
	32.0	11	gy	415
	33.8	....	g B P	475
VI. Mar. 28, 3d day.	34.0	13	g B P	470
	32.0	13	g y o bg	415
	30.5	12	w y b g	380
	29.8	8.0	w b r b	180
	28.8	6.5	w r g	110
	28.0	4.1	cor	24
	27.0	4.1	cor	24
Later...	30.5	10.6	y o g′	330
	28.7	6.3	cor	88
	27.1	3.4	cor	14
	25.6	3.4	cor	14
VII. Mar. 29, 4th day.	30.3	....	yo bg	330
	30.6	11	yobg	330
	30.6	9.4	w c g	230
VII. Mar. 30	30.5	11.5	yo bg	330
	30.5	10.7	w o g	300
	28.8	6.5	w r g	100
	29.6	10.5	w r g	25
	33.0	13	g B P	470
Later...	32.2	12	g B P	460
VIII. Mar. 31	30.8	11.5	g B P	460
	30.8	12.5	g y o	410
	29.6	11.5	y′ y bg	355
	27.7	5.2	w r	50
IX. Apr. 1	31.2	12	g B P	460
	31.2	13	gyo	410
Later...	30.6	12	gy o	410
	30.1	11	w y bg	375
X. Apr. 2	30.7	12	gy o bg	410
	30.6	12	y′ g bg	380
	30.6	7.8	w b r b	180
XI. Apr. 3	29.4	7.7	w P B	147
	29.5	5.8	cor	74
XII. Apr. 4	29.7	11	yo bg	300
	29.6	11	w o g	300
	28.8	8.8	w P B	220
	29.0	[2]8.3	w P ?	175
	28.0	6.0	cor	80
XIII. Apr. 6	33.9	[3]13	g B P	470
	26.5	3.9	cor	22
	26.9	3.9	cor	22
	27.6	5.2	cor	52
	28.8	8.9	w P	215
	27.6	7.3	w y	120
XIV. Apr. 7	27.5	7.4	w r g	120
	27.5	....	cor	....
	27.5	5.2	cor	52
	27.6	5.1	cor	49
XV. Apr. 8	27.2	[2]2.7	cor	7
	27.0	3.5	cor	15
	26.9	[4]3.5	cor	15
	25.5	3.0	cor	15
Series Apr. 8 (55)	25.2	1.3	cor	1.5
(56)	27.1	2.6	cor	6.4
(57)	28.9	5.9	wrg	78
(57′)	....	8.4	wP cor	210
(59)	32.5	12.5	w y g	390
XVI. Apr. 10 (58)	32.0	13	g B P	460
	30.8	13	gy o	455
XVII. Apr. 13	30.0	10.5	w r g	255
	30.6	9.5	w r g	240
Apr. 14	30.7	12.5	y g bg	380
	30.6	11.5	w o g	300
Apr. 15	30.9	13.	g y to g	455

---

[1] Alternate observations.

[2] Apparatus (fog chamber) *blurred*.

[3] After thorough cleaning.

[4] Warming with burner clears the glass.

while there is evidence of slight improvement, irregularities are at times increased. The final data in the table relate to the effects of X-rays from short distances ($D = 20$ cm. to anticathode), and the peculiar feature here is the steepness of the line as compared with earlier results. The reason is in part due to the admission here of $\delta p = p - p_2$ instead of the *observed* δp as heretofore, the effect being to displace upper observations relatively more to the left. It is already quite clear, however, that neither for X-air nor for ordinary air have the earlier data been much improved. The highest corona attained in both cases is again the green-blue-purple type.

TABLE 23.—Atmospheric air. Two observations daily. Water nuclei removed by low exhaustion. $\delta p = p - p_2$. Aug. diameter $s/30$ nearly. Fog chamber 40 cm. from eye, 250 cm. from light.

Date.	Observed.				Computed.	
	δp.	s.	Cor.	$n \times 10^{-3}$.	$p - p_2$.	$n \times 10^{-3}$.
May 17	30.6	....	g B P	450	23.7	385
	30.8	12	g B P	450	23.9	385
May 19	29.0	11	w y o g	320	22.5	270
May 20	28.8	11	w r o g	290	22.3	245
May 19	27.2	4.2	cor	27	21.1	22
May 21	27.4	3.6	cor	18	21.3	15
May 22	27.1	2.9	cor	8	21.0	7
Mar. 24; X-rays from $D = 20$.	33.6	....	g B P	....	26.0	410
	30.6	....	g B P	....	23.7	385
	27.9	....	g B P	....	21.6	360
	25.3	....	g B P	....	19.6	335
	21.7	5	cor	....	16.8	32
	21.6	5.0	cor	....	16.7	32
	22.5	10.5	w r g′	....	17.4	175
	23.5	....	g y o	....	18.2	290
	22.8	5.0	cor	....	17.7	34
	22.6	10.0	w y g	....	17.5	260
	21.5	3.6	cor	....	16.6	13
	21.6	3.7	cor	....	16.7	14
Mar. 26	21.5	3.8	cor	....	16.6	15
	23.7	11	gyo	....	18.3	290
	22.5	6.7	g B P	....	17.4	105
	22.6	8.7	wp cor	....	17.5	145
	25.5	....	g fog	....	19.8	335

50. Observations, continued.—In the experiments of table 22 much difficulty was experienced with the apparatus, as the use of oil with the large stopcock was often liable to show itself in the blurred walls of the fog chamber whenever this was wetted with water. It is usually sufficient to heat these walls gently, in order to evaporate the suspicion of an oil film which has here collected, after which the walls remain clear for some time on wetting. Prior to the systematic investigation of table 23, however, the apparatus was thoroughly overhauled and cleaned. The δp referred to is henceforth to be $p-p_3$, *i. e.*, the difference between atmospheric pressure and the pressure (p_3) observed when fog chamber and vacuum chamber are in communication at the given temperature.

Some time having elapsed since the last observation, the first experiments (parts I, II, etc.) of the tables show low nucleation, due to the presence of large nuclei originating internally, as already specified. Series III, with X-rays, agrees very fully with the preceding cases (table 22) and there is nearly the same steepness of curve ($\delta p = p - p_3$) already instanced. Conformably with this, series IV, V, etc., also show increased steepness of curve, the nucleation, moreover, being higher because the interior sources of relatively large nuclei have been gradually removed. But there is throughout much irregularity, and periods are frequent. Remembering that above the δp referred to is the drop of pressure observed in the fog chamber, while at present $\delta p = p - p_3$, a slight advance of the highest nucleations over the preceding cases is discernible.

51. Observations, continued.—In table 24 observations are recorded, made once or twice a day, far enough apart to allow water nuclei to vanish by time loss. After each measured corona a low exhaustion was (as usual) made to remove the greater number of such nuclei at once in the large particles of the small corona produced. The pressure difference (δp) is again $p-p_3$, as explained in section 48, so that the correction there adduced may be applied. The fog chamber was rigorously tight as regards the influx of external air, but air flowed slowly from fog chamber into the vacuum chamber, through the leaky stopcock. Between the exhaustions the air was kept at low pressure for about ten hours, and new air was admitted, just before exhaustion, through the filter into the fog chamber, until the barometer pressure had been reached. As the whole apparatus had been left standing a long time, dust-free air only was present in the fog chamber and vacuum chamber. The walls of the former were rubbed clean before beginning the work.

The table also contains the above data for air energized by the X-rays with anticathode distant 20 cm., observations being made while the radiation acted and immediately after the exposure began, to avoid the presence of persistent nuclei. The computed values for the drop in pressure ($p-p_2$, where p_2 is the computed isothermal pressure in the isolated fog chamber alone), and the corresponding values of n, are also given. The nucleation refers as usual to the exhausted fog chamber. The results are constructed graphically in fig. 33.

FIG. 33

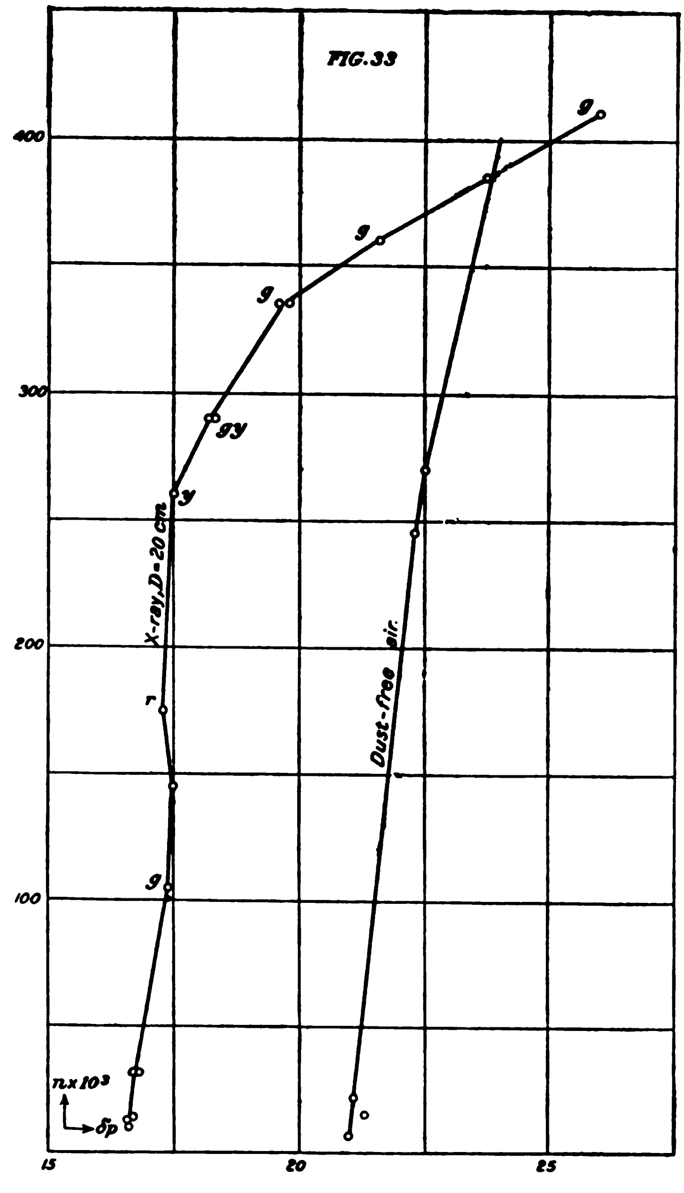


FIG. 33.—Nucleations (n) observed in dust-free air and dust-free X-air at different exhaustions (δp); 4-inch pipes. Table 23.

52. Discussion.—The new curves (fig. 33) lie nearer together for the energized and non-energized states of the gas. This obviously results from the correction applied to the observed values of δp. Neither do the graphs ascend as highly as they did before, for the same reason, remembering that the nucleation (n) always refers to the exhausted fog chamber. Again, the new curves must be steeper than the old; but both of them, *i. e.*, the curves for the non-energized and for the energized gas, have about the same slope, so far as can be made out for the case of such steep curves as those under consideration. Nevertheless, it is probable that there is some other reason implied in this, which is yet to be made out. For the ionized state the observations frequently suggest a kind of saturation beyond which the ions pass into persistent nuclei very much as a vapor condenses. In other words, a maximum ionization pressure, determined by a definite number of ions per cubic centimeter, which can be approached as the radiation is more and more intense, but not exceeded, is a useful conception in connection with many of the experiments given.

53. Summary.—The general summary of this chapter has already been given in sections 42, 43, and 52, particularly in the former, with regard to fig. 25, and need not, therefore, be repeated here. The highest order of available coronas has been invaded and surpassed.

It appears that the limits of efficiency of the practical fog chamber with rapidly opened plug cock have been reached when the long cylindrical vessel of about 6,000 c. cm. is exhausted into a vacuum chamber of about 100,000 c. cm. through a pipe not less than 5 cm. in bore nor more than 50 cm. long, with a stopcock of wider diameter (7 to 8 cm.) interposed. To test this again, such a fog chamber was adjusted as shown in fig. 34 (*V* vacuum chamber; *F* fog chamber; *G*, *g*, gages at the former and the latter, the whole mounted on casters to admit of shaking the water in *F;* goniometer attached to fog chamber). The results are given, both for fog chambers Nos. I and II, in tables 24 and 25, with corrections for the barometer as explained in Chapter VI, sections 100 and 101, and they are charted on a small scale with other data (table 23) in fig. 35.

The graph for chamber number II would coincide with data inferred from Wilson's colors for small coronas; but for large coronas it actually lies in a region of lower exhaustion—to which however, too much importance must not be attached, because of the difficulty of identification. The point is that the apparatus of 2-inch pipes is quite the equal, if not the superior, of the apparatus with 4-inch pipes, in the region of both the lower and higher coronas. Curiously enough, the apparatus I

(4-inch cock) gives an excess of ions, whereby the graphs for I and II in the region of lower coronas are consistently distinct. I will pass this over here, as it needs additional investigation.

That the limit of efficiency has been reached for plug-cock apparatus is specifically proved by the fact that the same large green-blue-purple corona terminates the observations, no matter whether the nuclei are relatively large, as in case of the ions and intense X-radiation, or relatively small, as in case of the colloidal nuclei. This is differently proved in the work with alcohol, in Chapter IV.

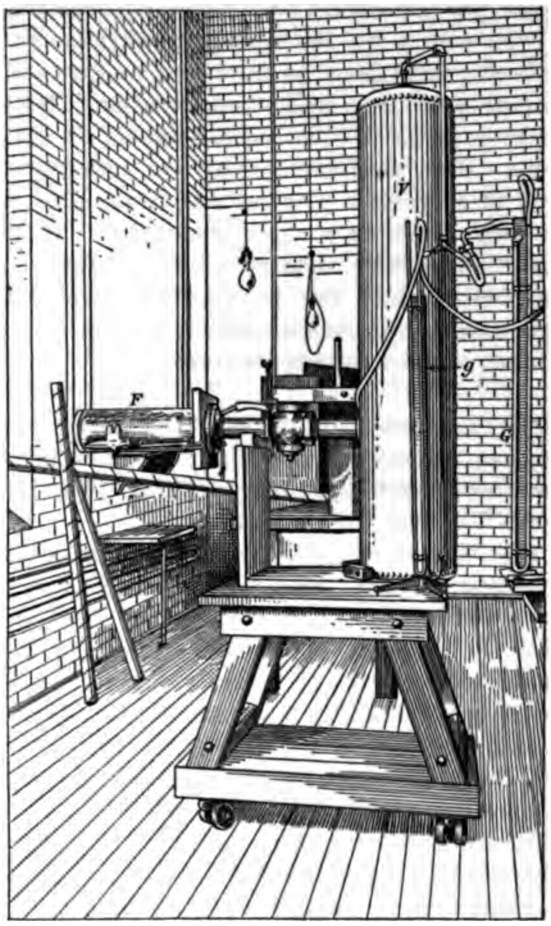


Fig. 34.—Disposition of apparatus in case of fog chamber (F) and vacuum chamber (V), connected by 2-inch pipes and 2½-inch stopcock.

It is somewhat hard to understand why the efficiency should terminate abruptly, with a certain *number* of nuclei per cubic centimeter, no matter whether large or small nuclei are in question. One should expect these conditions to depend on the size of nuclei; but (as the data show) even though larger numbers of nuclei are certainly present, they are devoid of efficiency beyond the limit.

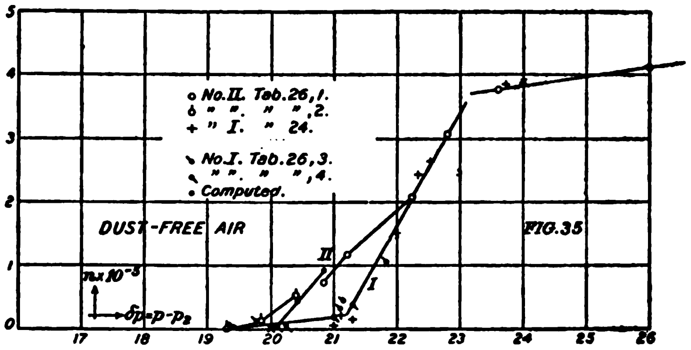


FIG. 35.—Nucleation (n, in hundred thousands of nuclei per c. cm.) observed in dust-free air and in energized air at different exhaustions. $\delta p = p - p_2$. 2-inch and 4-inch pipes and perfected apparatus I and II. Tables 23, 24, and 25. Ions in No. I consistently in excess.

TABLE 24.—Fog chamber and vacuum chamber as in fig. 34, joined by 2-inch pipes, 2½-inch plug stopcock. $\delta p = p - p_2$. Final series for comparison.

	δp.	s.	Corona.	$p - p_2$.	$n \times 10^{-3}$.	s corrected.*	$n \times 10^{-3}$ corrected.
I. Barometer 76.2	25.9	3.2	cor	20.1	9.5	3.4	11.6
	26.9	6.4	w p′ g	20.8	76	6.6	83
	27.4	6.8	g B P	21.2	120	....	....
	28.7	10.2	wr g′	22.2	210	....	....
	29.4	12	yr	22.8	310	....	....
	30.5	13?	g B P	23.6	380	....	....
	33.5	13?	g B P	26.0	410	....	....
II. Barometer 75.5	24.9	1.7	cor	19.3	1.8	1.3	1.4
	25.6	3.6	cor	19.8	15	3.2	9.9
	26.4	5.6	cor	20.5	53	5.2	42

TABLE 25.—The same; 4-inch stopcock, apparatus I.

	δp.	s.	Corona.	$p - p_2$.	$n \times 10^{-3}$.	s corrected.*	$n \times 10^{-3}$ corrected.
III. Barometer $p = 75.8$, July 14.	25.5	? 3.7	cor	19.7	15	3.6	....
	27.2	4.9	....	21.1	37	4.8	....
	25.0	2.4	....	19.4	4	2.3	....
	28.1	7.2	y′ b P	21.8	110	....	....
	27.3	5.3	....	21.1	45	5.2	....
IV. $p = 75.9$, June 3.	27.1	4.2	cor	21.0	22	....	....
	25.9	2.8	....	20.1	6	....	....
	26.1	2.7	....	20.2	6	....	....
	27.4	5.0	....	21.3	40	....	....

* Correction for barometer made as explained in Chapter VI.

In no form of the fog chamber have the initial yellows and browns of the steam jet been approached. Coronas reach but to the equivalent of the opaque zone. Below the large green-blue-purple corona, the computed value of the water precipitated per cubic centimeter may now be considered trustworthy. In Chapter I this was true below the middle green-blue-purple corona. The drop of pressure $(p - p_2)$ actually efficient in producing low temperatures in the fog chamber must be computed from the initial pressure of the isolated fog and vacuum chambers before exhaustion, and their final pressure when in communication after exhaustion, all data taken at the same temperature.

As the intensity of radiation increases, coarser nuclei become much more frequent, but beyond this the coronal method is not adapted to test the lower limit in question. At the upper limit, however, most of the observations show that the finer nuclei become more abundant when the medium is more powerfully energized; or that new gradations of nuclei of continually increasing smallness and continually increasing number are produced by radiation increasing in strength indefinitely. These are important questions, however, upon which I hope in the near future to make some final tests.

CHAPTER III.

MISCELLANEOUS EXPERIMENTS.

54. Objects.—Having perfected the coronal fog chamber to the degree specified in the earlier sections of Chapter II, it seemed expedient to make use of it for a variety of purposes partly corroborating and interpreting my earlier work, partly introducing new results. In particular, the growth of persistent nuclei in a highly ionized medium in the lapse of seconds, the occurrence of solutional nuclei, and like questions may be studied by the *depression* of the terminal asymptote produced by the introduction of relatively small numbers of larger nuclei into the medium. Again, the effects of radiation from different distances on the medium of the fog chamber, the absorption of such radiations, the distributions within the fog chamber, etc., may be elucidated by this treatment. Finally, some consideration of the rates of generation and decay of ions is in place and a method will be shown for the standardization of coronas. Some final remarks will be made on the steam jet and on the relation of its color phenomena to those of the fog chamber.

Throughout this chapter δp refers to the drop of pressure observed at the isolated fog chamber under isothermal conditions, the exhaust cock being closed as soon as possible after the expansion. The necessary reductions (should they be needed) may be made as shown in the preceding section.

55. Growth of persistent nuclei.—In table 26 (illustrated by fig. 36) the time during which the fog chamber was exposed to the X-rays, with the anticathode at a distance of $D=10$ cm. from the fog chamber, is given in the first column. The coronas and the number (n) of nuclei per cubic centimeter follow.

The two series of experiments made show that there is a gradual increase of the number of persistent nuclei, evidenced by the gradual reduction of the number of efficient nuclei. In less than two minutes, however, the phenomenon becomes more stationary, indicating that the full number of persistent nuclei is being approached, or that there are now about as many made as are unmade per second. It is difficult to follow the phenomenon beyond this, for the coronas now become campanulate or otherwise distorted, appearing in association with heavy fogs. The true asymptote is probably far off. These data furnished good illustrations bearing on the remarks of section 42, Chapter II.

TABLE 26.—Persistent nuclei produced after different lapses of time. Method, depression of asymptote. $\delta p = 26.4$ cm.; $D = 10$ cm. above side of cylindrical glass fog chamber; cock 1½ inches; exhaustion during exposure.

Exposure.	s.	Corona.	$n \times 10^{-3}$.
sec.			
0	13	g B P	410
30	12	w y g′	340
60	11	w o g′	270
90	7.5	(1)	140
120	7.6	(1)	140
30	13	w y g′	340
60	11	[1]w r g	230
90	9	(1)	200
0	14	g B P	410

[1] Tempestuous fog and rain, leaving smaller corona. Second exhaustion made for safety, showing small corona.

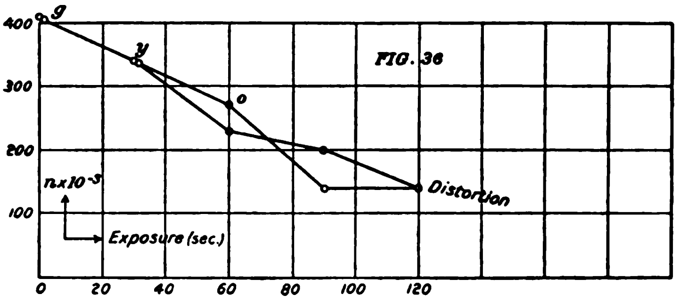


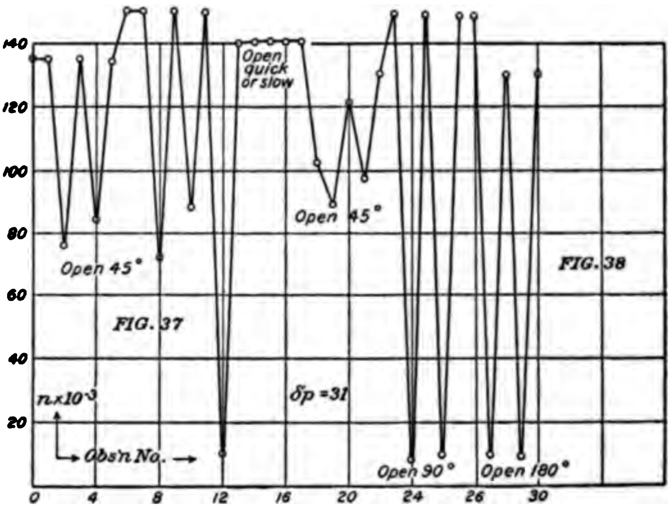
FIG. 36.—Depression of efficient nucleation (n) of dust-free air ionized by strong X-rays at a given exhaustion, by accumulation of persistent nuclei in the lapse of time. Table 26.

56. Water nuclei produced by evaporation.—A beautiful method of demonstrating the production of water nuclei in connection with the condensation of fog consists in leaving the cock for influx of air from the filter slightly open. In such a case the fog begins to evaporate as soon as produced, and there will be less loss from subsidence of fog particles, in proportion as the evaporation is more rapid; in other words, as the stopcock is more widely opened. Table 27 shows results of this kind and they are reproduced in fig. 37, where the abscissas are distributive. In every case the efficient nucleation (n) of dust-free air, after complete subsidence of the preceding fog, is much in excess of n', the nucleation observed when the fog is dispelled by evaporation. The table also proves that the degree to which the filter cock (fine screw valve) is open does not influence the result.

TABLE 27.—Enlargement of nuclei of dust-free air. Glass fog chamber, single wet cloth partition. $\delta p = 30.9$ cm.; s found after complete subsidence of preceding corona; s' after partial subsidence with evaporation.

Date.	s.	s'.	Cock open.	$n \times 10^{-3}$.	$n' \times 10^{-3}$.	s.	$n \times 10^{-3}$.	Remarks.
			°					
Oct. 17	[1]7.0	...	45	135	..	[3]7.4	140	Full subsidence but with quick opening of cock (90°) thereafter.
	[2]7.0	...	45	135	..	7.4	140	
	...	5.8	45	...	76	7.5	140	
	7.0	...	45	135	..	...	...	Same, but with slow influx.
	...	6.0	45	...	84	7.4	140	
Oct. 19	7.1	...	45	135	..			
	[4]7.3	...	45	150	..			
	7.3	...	45	150	..			
	...	[5]5.7	45	...	72			
	[4]7.4	...	45	150	..			
	...	[5]6.2	45	...	88			
	[4]7.5	...	90	150	..			
	...	[5]3.0	90	...	10			
	[3]7.2	...	90	140	..			

[1] After many days' waiting.
[2] w o g.
[3] After few minutes' waiting.
[4] g B P.
[5] Blurred with much rain.



FIGS. 37 and 38.—Periodic variation of efficient nucleation (n) in case of an open filter cock. Tables 27 and 28.

In table 28 and fig. 38 the occurrence of periodic variation in the angular diameter of successive coronas and the corresponding efficient nucleation is shown by the same method of a permanently opened filter cock. The conditions of all of the exhaustions are quite identical; but the small fog particles of large coronas evaporate faster and in greater numbers than the larger particles of smaller coronas. Hence the water nuclei are present in like periodic distribution. The effect is more striking when the stopcock is opened wider. The difference between 180° and 90° in the adjustment of the cock is not marked, because the filter itself introduces resistance to flow.

TABLE 28.—Corresponding to table 27. Periodicity due to permanent open filter cock.

	s.	*s′*.	Cock open.	*n*.	*n′*.
			°		
Oct. 20 ..	..	[1]6.5	45	..	102
	..	[2]6.2	45	..	89
	..	[1]6.9	45	..	121
	..	[2]6.4	45	..	96
	..	[1]7.1	45	..	130
	..	[1]7.5	90	..	150
	..	[3]2.8	90	..	7.8
	..	[4]7.2	90	..	150
	..	[3]3.0	90	..	10.0
	..	[4]7.2	90	..	150
	..	[4]7.4	180	..	150
	..	[3]3.0	180	..	10
	..	[1]7.0	180	..	130
	..	[3]2.9	180	..	9
	..	[1]7.0	180	..	130

[1] w o g.

[2] w r g. Note the periodicity of the series.

[3] Blurred with rain.

[4] g B p.

TABLE 29.—Corresponding to table 27. Effect of δp; cock open during exhaustion.

	δp.	*s′*.	Cock open.	*n′*.
			°	
Oct. 22	26	3.6	45	17.1
	26	2.6	45	6.3
	26	2.7	45	7.1
	28	5.9	45	77
	28	4.4	45	31
	28	5.2	45	53
	30	7.0	45	125
	30	6.1	45	85
	30	6.9	45	120
	30	6.0	45	85
	30	6.6	45	105
	..	7.3	Closed	135

In table 29 the effect of different drops of pressure (δp) is investigated for low exhaustions and smaller coronas and there is scarcely any periodicity. As the exhaustion is higher, periodicity in the size of successive coronas is correspondingly marked. The data give an estimate as to the degree in which periods are to be guarded against.

In table 30 experiments similar to the preceding are made with ionized air. It will be seen that the periodicity is in every case just as marked as before. In the absence of evaporation (closed filter cock) the successive coronas are equal. Precipitation at a low drop (δp) of pressure is followed by a relatively large corona at a higher drop of pressure, as the water nuclei have been removed in the former.

TABLE 30.—Periodicity of ionized air. X-rays; $D = 50$ cm. Filter cock permanently just open. Exhaust cock 2½″; $\delta p = 23$ cm. below fog limit of dust-free air.

Exp. No.	*s.*	Cor.	$n \times 10^{-3}$.
1	10.5	w r g	210
2	6.3	cor	75
3	9.6	w c g	200
4	5.0	cor	41
5	10.4	w r g	210
6	5.6	cor	58
7	9.2	w c g	190
Filter cock closed during exhaustion and subsidence.			
8	[1]9.3	w c g	190
Dust-free air not energized; $\delta p = 31$; repetitions without waiting Dec. 13; internal evolution of nuclei has ceased.			
....	11.5	w y g	335
....	11.5	w y g	335
Dust-free air not energized; $\delta p = 36$ cm.			
....	13.5	g | P	480
....	13.5	g | P	480
Evap. nuclei precipitated at $\delta p = 23.2$ cm. and then tested at $\delta p = 31$.			
1	3.0	cor	8
2	0.0	—	0
3	—	[2]g y o	410

[1] No difference between 7 and 8.

[2] Corona enlarged by the preceding precipitation.

Some interesting questions present themselves in connection with this work. Are the nuclei holding positive ions different from those holding negative ions? Do they retain their charges, or some equivalent of the charges? As there is less mobility and slower recombination in cases of ions entrapped by water nuclei, one would infer greater opportunity for the gravitational separation of the equivalents of the positive and negative charges; for it seems improbable that the water nuclei resulting can be of the same size.

Finally, in table 31 data have been gathered showing the gradual self-purification of the fog chamber, after cleansing and sealing. Nuclei arising from some internal source cease to appear in the mere lapse of time and without further interference. The coronas s_1 and s_2 are observed in successive exhaustions at the time (days and hours) given. Initially the first corona is smaller in marked degree, owing to the spurious nucleation within. After more than three days, however, both coronas s_1 and s_2 are identical.

TABLE 31.—Purification of the fog chamber in the lapse of time. $\delta p = 31$. Exhaust cock $2\frac{1}{2}$ inches; piping 12 inches long, 2 inches in diameter.

Date.	Hour.	s_1.	Cor.	s_2.	Cor.	$n_1 \times 10^{-3}$.	$n_2 \times 10^{-3}$.
Nov. 30	10 a. m.	4.6	......	11.5	......	40	305
	5 p. m.	7.5	g B P	12.0	w y g′	150	380
Dec. 1	10 a. m.	8.0	w P cor	11.7	w y g′	180	380
	6 p. m.	[1]9.7	w c g′	....	g y o	275	410
Dec. 2	......	9.2	w r g	11.4	w o g	230	305
13	......	11.5	w y g	11.5	w y g	305	335
	......	[2]14	g′	14	g | P	460	460

[1] Vacuum maintained some hours. [2] $\delta p = 36$. Internal source of nucleation absent.

The source of this transient internal nucleation is difficult to detect. There were no leaks. Oil evaporation if harmful would be continuous. The same differences of fresh and stagnant air in relation to s_1 and s_2 are always reproduced. There is no evidence that anything in the vacuum chamber is capable of diffusing into the fog chamber. Some agency therefore, which is productive of relatively large nuclei, and the nature of which is not clear, survives many consecutive precipitations.

57. Distance effects. X-rays.—In the following experiments I endeavored to overhaul the curious results obtained when the X-rays strike the fog chamber from different distances, without, however, reaching very satisfactory conclusions. The object of the following work is to bring to bear the newly improved means on the problem. In table 33 data are given as obtained with the glass fog chamber, the drop of pressure (δp) being below the coronal fog limit of dust-free air. Hence there are no complications from colloidal nuclei. In parts I and II of the table the X-ray bulb was not inclosed in the windowed lead vessel specified, whereas in part III this is the case; while in part IV a tin plate has been placed over the window.

TABLE 32.—Distance effects due to X-rays. Fog chamber of glass with 2.5-inch gas cock and 2-inch piping 12 inches long. X-ray, 7 cells. $\delta p = 23.8$ cm.

	D.	*s.*	Corona.	$n \times 10^{-3}$.
I. Bulb not inclosed; meters........	0.5	10.0	w c g	220
	6.0	6.3	cor	80
	...	6.2	......	75
	2.0	7.3	w′ B P	115
	...	7.4	w′ B P	120
	.5	11.0	g y o	260
$\delta p = 20.3$ cm.				
II. Same; bulb not inclosed........	0.5	...	w B P	90
	...	7.2	w B P	100
	2.0	5.2	......	42
	...	5.2	......	42
	6.0	3.5	......	13
	...	3.5	......	13
	4.0	3.6	......	15
	...	4.5	......	28
	1.0	6.4	w r g	75
	...	6.3	w r g	70
	.5	7.2	w y g	100
		7.3	w y g	105
$\delta p = 22.7$; X-ray bulb in lead case[1] with window 7.5 cm. in diameter.				
III. Window open.................	600	4.1	cor	22
	400	4.4	cor	27
	200	6.5	w r g	85
	100	7.5	g B P +	135
	...	7.5	g B P +	135
Lid off.......................	...	7.5	g B P +	135
Same. Tin plate[1] over window.				
IV. Tin window	600	2.7	cor	6.5
	200	4.9	cor	40
	100	6.9	w r g	99

[1] Lead sheet 0.12 cm. thick; tin plate 0.03 cm. thick.

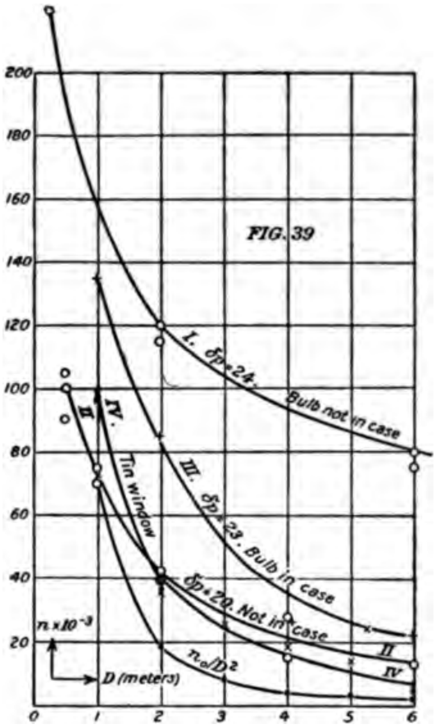


FIG. 39.—Nucleation (ions) produced by a radiating X-ray bulb (cased in lead or not as stated), at different distances (D) from the glass fog chamber. Table 32.

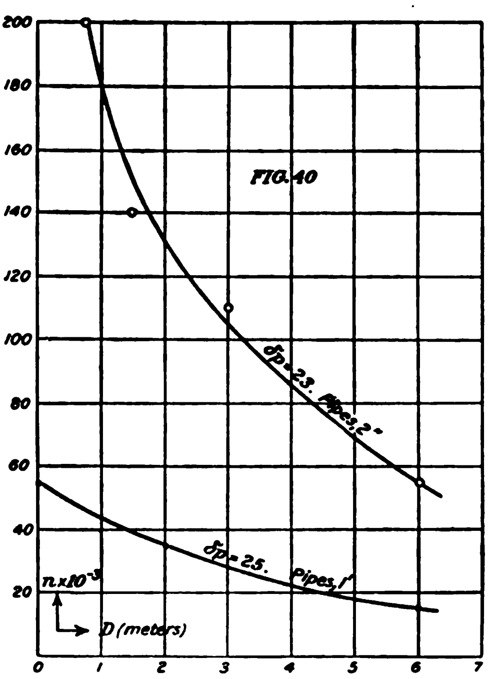


FIG. 40.—The same, illustrating table 15, Chapter II.

The curves I and II, fig. 39, for the free bulbs show different nucleations, compatibly with the different values of δp applied, but are otherwise alike in character. They in no way suggest the law of inverse squares. The curves III and IV for the inclosed bulb are again similar in character, but beyond this very little can be stated. If in case of series II and III, for instance, the law

$$n\,(A+D)^2=\text{const.}$$

is assumed, the constant A would have to be from 1.2 to 2.7 meters in the first case, and 1.5 to 2.1 meters in the second, which is entirely out of the question for a fog chamber less than 0.5 meter long. If the law

$$n\,(A+D)=\text{const.}$$

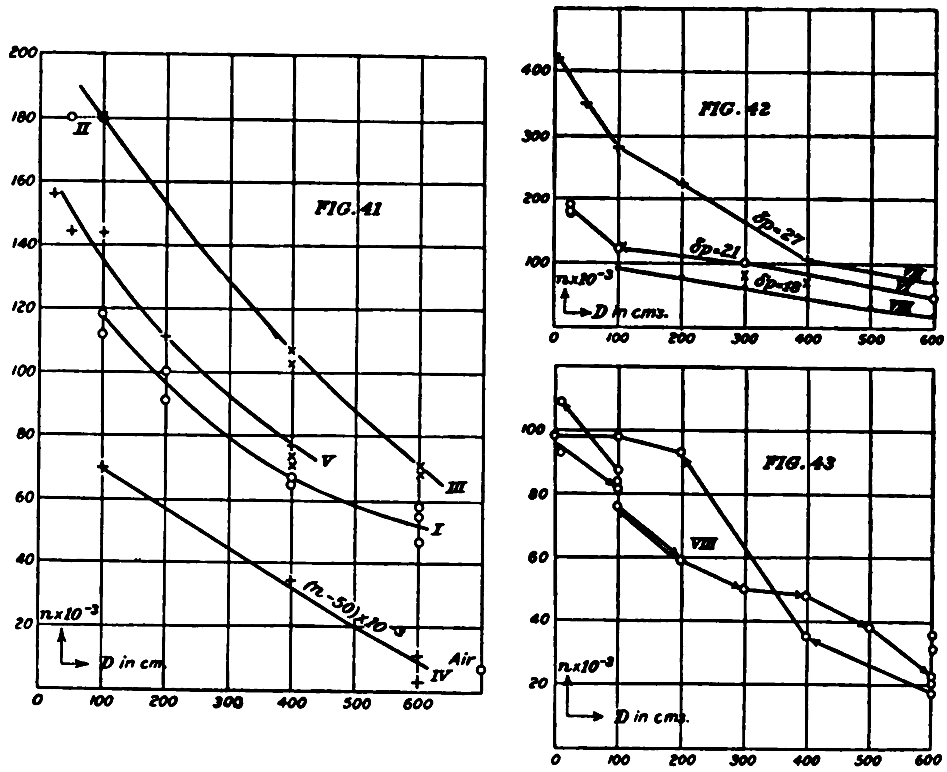
is used, in the first case (II) $A=0.3$ to 0.1 meter; in case III, $A=-0.2$ to -0.6 meter. This decrease would then be too fast in the first case and too slow in the second, or the decrement in case of the open bulb is slower and in case of the inclosed bulb (lead box with window) faster than the first power of distance.

In fig. 40 I have inserted data incidentally obtained in Chapter II, table 15 (upper curve), together with data of the same kind in the earlier reports (lower curve). The former are the steepest curves obtained and the latter the least so. Here, as elsewhere, it is difficult to conjecture a reason for this apparently erratic difference of behavior, unless it be referred to the facility with which secondary radiation is evoked, and to the degree in which the fog chamber is pervious to it or generates it. Since $dn/dt=a-bn^2=0$, where a is the number of ions produced per second, a must vary as the square of the number of ions, n, observed.

58. The same, continued. Small wood fog chamber.—The data of the last paragraph with the glass fog chamber suggest a comparison with the wood fog chamber. The latter is much the more pervious and in the earlier work showed a much smaller distance effect. Table 33 contains eight series of results. In series I, fig. 41, the march is not unlike the case for the glass chamber; but in series II the insignificant difference between a bulb distance of 50 and 100 cm. from the fog chamber (curves III and IV) are similar to I, and often betray the incidental weakening of the X-ray bulb. In the series VI to VIII, change of the drop of pressure (δp) was introduced, but the inherent difficulty of coping with the bulb variations is seen in the details in fig. 43.

It is probable that the ordinates of the curves V to VIII (figs. 42 and 43) are proportional to each other; but a discussion is beyond my present purpose. The slow order of change with distance should, however, be noticed.

59. The same, continued. Large wood fog chamber.—It is with this apparatus that the coronas of almost the same aperture were obtained in the earlier work, while the X-ray bulb was moved from 1 to 6 meters from the fog chamber. Table 34 and fig. 44, however, show that this result must have been due to other conditions, for there are changes of nucleation here registered amounting in case of the distance specified (1 to 6 meters) to $n'/n=145/104$ at $\delta p=22$; $77/41$ at $\delta p=19$. For greater pressure differences, $\delta p=25$ and 29, the occurrence of terminal coronas would interfere with the comparisons. At higher exhaustions still, the efficiency of air nuclei would be gradually restored, so that the observed nucleation may be greater with the bulb at 6 meters than at 1 meter from the fog chamber (see Chapter II, figs. 24 and 25). At the very low exhaustion $\delta p=17$ the coronas are too small to be serviceable for comparison.



Figs. 41, 42, and 43.—Nucleations (ions) produced by a radiating X-ray bulb at different distances (D) from the small wood fog chamber. Table 34.

With regard to the work of table 34 it should be stated that it is always customary to make a second exhaustion to remove the water nuclei left by the first. Again but two distances (1 and 6 meters) were selected to guard against losses of efficiency of the X-ray bulb, so far as possible. The exhaustion was made during the exposure, which was always brief. At the distance $D=6$ meters from the bulb, there is a terminal corona at $\delta p=22$ cm.; at $D=1$ meter it appears a little later at $\delta p=25$. (See Chapter II, figs. 24 and 25.) In fig. 45 the corresponding points are joined by straight lines, for convenience.

60. The same, continued. Discussion.—Experiments of the present kind are hampered by two annoying difficulties, the first being the variability of the X-ray bulb, the other the tendency of the wooden fog chambers to develop slight leaks which often pass unobserved. True, the chamber is tested by a second exhaustion after each of the coronas measured; but the unfiltered atmosphere entering anywhere is liable to produce a disproportionate amount of distortion, because of the relatively large size of the nuclei contained. Hence it is of little value to attempt to systematize the above results in the absence of a well-digested

TABLE 33.—Revision of distance effect. X-rays. Small wooden fog chamber 15 × 11 × 45 cm. $\delta p = 21.7$ cm.

	D.	*s.*	Corona.	$n \times 10^{-3}$
I.	*cm.*			
X-rays off	....	[1]2.9	.....	7
X-rays on	[2]100	9.0	w r g	180
	600	5.3	.....	47
	600	5.6	.....	55
	600	5.7	.....	58
	400	6.1	w y′	67
	400	5.9	w r	65
	200	7.0	g′ B	100
	200	6.8	g′ B P	91
	100	7.4	.....	112
	100	7.6	w r	118
	100	7.4	.....	112
II.				
X-rays off	....	2.8	.....	7
X-rays on	100	[2]9.2	w r g	180
	50	9.2	w r g	180
	50	9.2	w r g	180
	100	8.7	w r g	180
	100	9.2	w r g	180
III.				
X-rays on	100	9.2	w r	180
	400	7.1	w y	103
	400	7.2	w y	106
	600	[3]5.6	cor	55
	600	6.2	.....	71
	600	6.1	.....	68
Bulb weaker	400	6.3	g′ B P	74
	400	6.2		71
IV.				
X-rays on	200	7.6	g B P	120
	400	6.6	g′ B P	85
	600	[3]4.4	.....	26
	600	5.5	w r g	53
	600	5.8		61
V.				
X-rays on	400	6.4	w b r	77
	200	7.4	w r	112
	100	7.9	w p	144
	50	7.9	w p	144
	25	8.5	wp′ g	156
VI.				
X-rays off	....	[4].0		0
X-rays on	25	9.6	w r g	190
	25	9.0	w p	175

	D.	*s.*	Corona.	$n \times 10^{-3}$
VI.	*cm.*			
X-rays on	25	9.0	wp	175
	100	8.0	w B P	120
	100	7.8	w B P	120
	300	7.3	w r o g	100
	300	7.3	w r o g	100
	600	5.4	w r g	50
	600	5.2	.....	45
High $\delta p = 27.5$.				
VII.				
X-rays off	....	[5]4.6	.....	6.5
X-rays on	600	5.8	.....	70
	400	6.7	w y′	105
	200	9.5	w r g	225
	100	11.0	w y o g′	280
	50	11.5	w y g	350
	10	....	g y o ?	420
VIII.	10	5.9	w y′	59
	....	7.6	w r	93
	100	7.2	w r	87
	10	7.4	g′ B P	109
	100	7.5	w y g′	84
	600	[6]4.1	cor	18
	....	[6]4.7	cor	31
	....	[6]5.0	cor	35
	400	[6]5.0	cor	35
	200	7.0	w r g	93
	100	7.6	w y g	98
	20	7.6	w y g	98
	100	7.3	w r g	82
	200	5.9	w r g	59
	300	5.6	cor	50
	400	[6]5.5	.....	48
	500	[6]5.1	.....	38
	600	[6]4.2	.....	21
	600	[6]4.3	.....	23
	100	[6]6.4	w r g	76

[1] $\delta p = 25.3$, $s = 5.7$. [2] Fresh bulb. [3] Battery current weak.

[4] Second exhaustion without rays made (after the first) to remove water nuclei.

[5] $\delta p = 28.1$, $s = 48$, $n = 57,000$; $\delta p = 29.7$, $s = 5.2$, $n = 55,000$; $\delta p = 31.9$, $s = 5.6$, $n = 71,000$.

[6] Coronas large on the near end and small on the far end of fog chamber. Subsidence oblique.

TABLE 34.—Revision of distance effects. Large wood fog chamber. 20×12×55 cm. Exhaustion during exposure.

	D.	s.	Corona.	$n \times 10^{-3}$.
$\delta p = 19.0$ cm.				
X-rays off	...	1.2	just seen	1.2
X-rays on	600	5.3	.....	43
IX.	600	4.5	.....	26
	100	6.6	.....	77
	600	5.2	.....	41
	600	5.1	.....	39
	600	4.0	.....	18
$\delta p = 21.8$ cm.				
X.	600	5.6	.....	56
	100	8.7	w p	145
	100	8.8	w p	145
	600	6.6	w r′	103
	600	6.5	w y	103
$\delta p = 25.1$ cm.				
XI.	600	6.5	w o g	112
	100	9.5	w r o g′	236
	600	7.0	w y	119

	D.	s.	Corona.	$n \times 10^{-3}$.
$\delta p = 17.1$.				
XII.	600	1.0	.....	1.0
	100	2.8	.....	5.3
$\delta p = 24.8$.*				
XIII.	100	9.5	w r o g′	236
	$\delta p =$	27.6		
	100	10.0	w r o g	254
	$\delta p =$	29.4		
	100	^{1}10	w r o g	265
	600	6.2	w r g	110
	100	10	w r o g	265

* Terminal corona; same for 7 and 9 cells.

theory of the phenomena; but the equations $n = n_0/(A+D)^2$ and $n = n_0/(A+D)$, where A is constant and D the distance between bulb and fog chamber, may be adduced to accentuate the order of values observed. This has been done in case of table 32, showing that for the non-incased bulb even the inverse first power of D varies more rapidly than the observed phenomenon. To a much greater extent is this true for the wood fog chambers. The phenomenon itself is clearly a case of superposition of primary and secondary radiation. The latter, moreover, is furnished not only by the environment of the X-ray bulb, as shown in fig. 39 by surrounding the bulb with a windowed lead case, but also by the immediate environment of the fog chamber. The small distance variation encountered would then seem to be explained by supposing that relatively much secondary radiation is released by relatively weak primary radiation, as compared with a case of strong primary radiation. Under all circumstances the total effect is an integral to be extended over the whole surface and possibly the interior of the room. Finally, one should recall that the rate at which ions are produced by the radiation must vary as the square of the number observed.

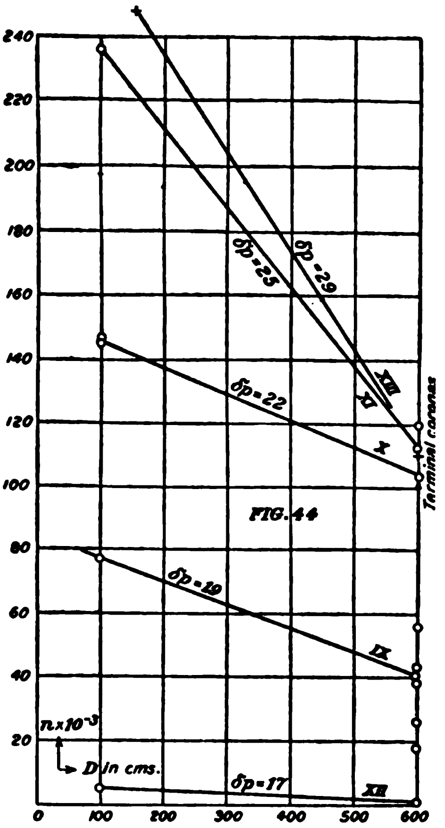


FIG. 44.—Nucleations (ions) produced by a radiating X-ray bulb at different distances (*D*) from the large wood fog chamber. Table 34.

61. Distance effect and absorption. Radium.—A few experiments were made incidentally with impure radium (10 mg. 10,000×, sealed in aluminum), using the method of depression of the terminal asymptote. In table 36, for instance, results are recorded on the absorption of the γ-rays in lead. Fig. 45 shows the results in relation to the nucleation of dust-free air, the efficient nucleation of which is more and more reduced as the intensity of the radiation increases with the diminishing thickness of the absorbing lead envelope.

After nearly 1.6 cm. of lead have been penetrated, the distance of the curve from the asymptotic air line is still marked. Results of this kind should furnish valuable data for testing any theory on the distribution of precipitated moisture on graded nuclei under any definite conditions.

Table 36 gives an incidental series of distance effects worked out by the same methods. As exhibited in fig. 46, the first series reaches the

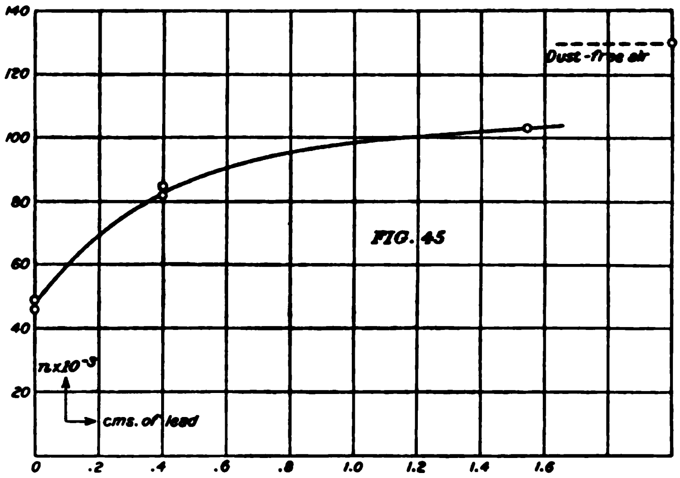


FIG. 45.—**Depression of efficient nucleation (*n*) of dust-free air, ionized by gamma-rays of radium penetrating through different thicknesses of lead. Table 35.**

high asymptote for dust-free air practically at a distance of $D = 150$ cm. In the second series the asymptote is lower, due to details in the adjustment in the apparatus, and reached later, *i. e.*, at a distance of $D = 180$ cm. between the radium and the fog chamber. This curve has been worked out completely for $D = 0$ cm., and shows the very interesting feature of a well-developed minimum. In other words, as the radium is removed from the fog chamber, the ions which at first predominate and capture all of the moisture decrease more and more in number, until the conditions are ripe for the simultaneous condensation of moisture on the colloidal nuclei of dust-free air. In proportion as the radium is further removed, the latter predominates, fully so when the asymptote is reached.

TABLE 35.—Absorption of lead. γ-rays of radium 10,000 ×. $D = 100$ cm.; $\delta p = 31$ cm.

Thickness t.	s.	$n \times 10^{-3}$.
∞	7.2	131
1.54	6.0	85
	6.5	103
	6.5	103
0.40	6.0	85
	5.9	82
.0	4.9	49
	4.8	46
∞	7.0	128

The corresponding results when the radium tube is inclosed in a thick lead pipe (walls 5 mm., length 60 cm.) shows a much sharper minimum, occurring at lower exhaustions. Such irregularities as are apparent here may be referred to the unequal distribution of radiation within the fog chamber discussed in Chapter I, sections 4 *et seq.* All of these curves have a similar bearing on the question of the distribution of the precipitate of graded nuclei.

TABLE 36.—Distance effect and absorption of radium rays. D measured from side. $\delta p = 31$. November 2. Lead pipe 0.5 cm. thick, 60 cm. long

	D.	s.	$n \times 10^{-3}$.		D.	s.	$n \times 10^{-3}$.
	cm.			III.	cm.		
II..........	180	6.2	90	In lead pipe..	145	5.6	70
	150	5.9	82		100	4.7	42
	100	4.7	42		50	4.3	32
	50	3.7	21		25	4.1	27
	25	3.7	21		10	4.0	24
	10	4.7	42	On top......	1	4.9	49
Above fog chamber...	2.2	4.8	46	At ∞	...	7.2	135
On glass.....	0	5.6	70				
	350	6.7	111				
	300	6.8	116				
	250	6.2	90				

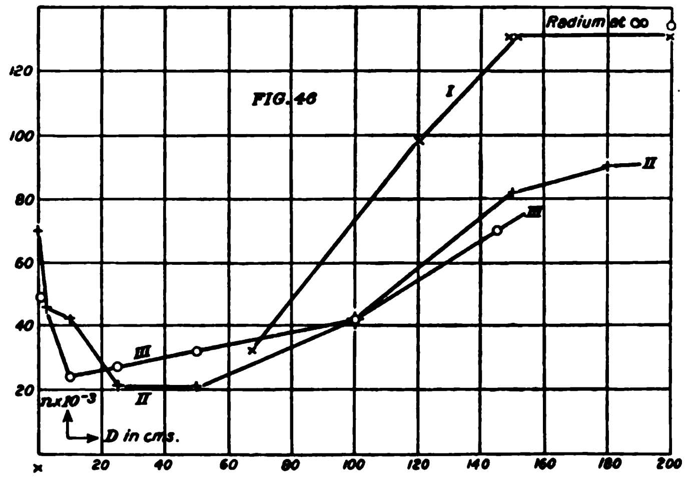


FIG. 46.—Minima of efficient nucleations observed at high exhaustions with radium at different distances (D) from the fog chamber. Table 36.

62. Falling to pieces of ions in the lapse of time.—Miss L. B. Joslin contributes the following interesting observations obtained by the method of depression of the terminal asymptote.

The data summarized in table 37 and fig. 47 were obtained by acting, in the manner stated, on the dust-free moist air contained within a glass fog chamber, with a sample of weak radium (10,000×, 10 mg.), sealed in an aluminum tube. This was placed on the outside of the chamber in contact with its walls (0.2 to 0.3 cm. thick), and was then removed suddenly at given intervals before exhaustion. Only very penetrating primary rays (β and γ) are therefore in question. The curves show the number of efficient nuclei in thousands per cubic centimeter, observed after the lapses of time shown by the abscissas, and it is supposed that the nuclei are reproduced faster than they can be removed by the exhaustion. In the upper curve the pressure differences applied ($\delta p=31$) are much above the fog limit of dust-free air, which is below $\delta p_0=24$ for the given apparatus. In the lower curve the pressure differences are nearly at the fog limit of dust-free air, while the other curve ($\delta p=28$) applies for intermediate conditions. The effect of the radiation is therefore, virtually at least, a coagulation (to use a figurative expression) of

TABLE 37.—Falling to pieces of ions produced by radium. Everything ready; cocks closed before removing radium.

Date.	t.*	s.	Cor.	$n\times10^{-3}$.
$\delta p=31$ cm.				
	sec.			
Oct. 19	∞	7.4	w′ o bg	140
	0	5.8	cor	76
	15	4.0	cor	24
	30	5.0	cor	51
	60	5.9	c o y g	82
	90	6.7	w o g	111
	120	7.2	w o g	134
	180	7.5	w o g	145
$\delta p=24.5$ cm.				
Oct. 24	0	6.3	....	79
	5	5.1	w r g	45
	10	4.7	w r g	36
	15	3.7	....	18
	20	3.6	....	16
	25	3.2	....	11
	30	2.3	....	3.5
	5	4.8	w o g	45
	10	4.2	w r g	29
	12.5	3.9	w r g	23

Date.	t.*	s.	Cor.	$n\times10^{-3}$.
$\delta p=28$ cm.				
	sec.			
Oct. 25	0	5.8	w r g	72
	15	3.8	w o g	21
	30	3.5	....	16
	45	3.3	....	13
	60	3.4	....	14
	120	4.7	....	40
	180	4.6	....	37
	∞	4.6	....	37
	∞	4.8	....	43
Oct. 27 Repeated. Decay of ions at $\delta p=24$.				
Radium on.....		60	2	2.5
Radium at ∞...		...	1.3	1.6
Radium on.....		30	3.3	12.1
		†30	3.2	11.4
		15	4.2	25
		10	4.7	36
		0	6.2	77
Fog limit of air. Radium off.				
$\delta p=23.6$.............			1.3	1.5
$\delta p=22.6$.............			.0	.0

* Seconds elapsed after removal of radium.

† First coronas dense but fall out rapidly, leaving fainter and *smaller* coronas behind.

the colloidal nuclei of dust-free air into the aggregates much larger in size representing the ions. Hence in the presence of radium under the given conditions the number of *efficient* nuclei decreases either because the ions from their size capture all the available moisture more and more fully, or because the colloidal nuclei have actually been aggregated into fewer but larger systems, which will in turn fall apart in the absence of radium.

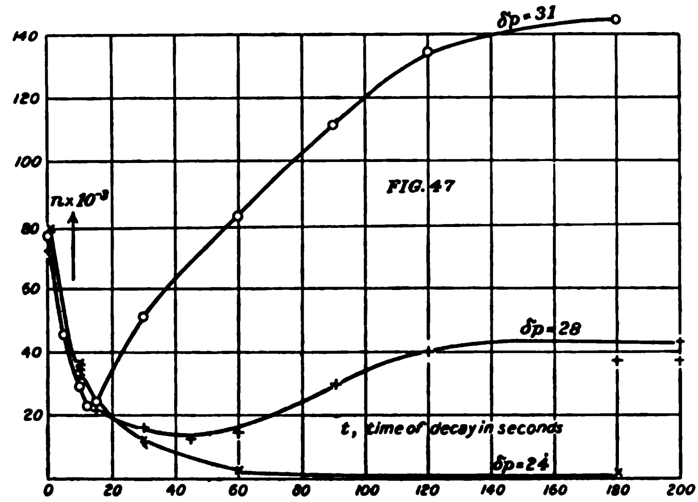


FIG. 47.—Efficient nucleation observed within the fog chamber at different times after exposure to radium applied outside at different exhaustions (δp). Table 37.

It follows from what has been stated that above the fog limit of dust-free air the number of efficient nuclei must increase with the removal of radium at a rate which corresponds to the falling to pieces of the ions. The peculiar feature of the results here in question is the manner in which the efficient nucleation decays from the coarser ionized to the finer non-ionized colloidal stages, when the pressure difference is decidedly above the fog limit of air, so that the latter may be recognized. The curves invariably pass through a minimum when the time after the removal of the radium, *i.e.*, the interval of decay, increases indefinitely.

This minimum, moreover, is very sharp, almost cusp-like, as if one law were passing abruptly into another. Thus below the minimum ($t = 13$ sec., about) the curve for $\delta p = 31$ nearly coincides with the curve for $\delta p = 24$, which is practically independent of the colloidal nuclei of air. The decay may be computed to be of the order of that of ions. After a lapse of 13 seconds the effect of colloidal nuclei is marked for $\delta p = 31$; and even after a lapse of 60 seconds, when the ions (lower curve) have vanished to a few hundred, the upper curve is only half way on its march toward the asymptote. This shows the remarkable sensitiveness of the method as a test for the presence of ions or of any nuclei larger than the colloidal sizes. Moreover, measurement of the large coronas is relatively easy. Finally, the curve $\delta p = 31$, if prolonged backwards, would seem to start nearly from the origin; in such a case one would have to picture to oneself a single particle breaking to pieces, in the absence of radiation, into fragments of continually decreasing size, until the débris ultimately numbers 150,000 colloidal nuclei.

The intermediate curve ($\delta p = 28$) also coalesces* approximately with the other curves for lapses of time less than $t = 13$ seconds. It has its own minimum, however, and from the lower pressure difference, necessarily its own asymptote at $n = 40,000$, since only the coarser order of air nuclei fall within the given limits of condensation in the apparatus used. For the same reason the minimum is lower and later, seeing that the ions are present throughout in relatively greater numbers as compared with the efficient colloidal nuclei, than was the case at $\delta p = 31$.

The curves as a whole have so close a resemblance to the data investigated in section 61 for the effect of radium at different *distances* from the fog chamber that the same cause must underlie both series of observations. In the former case (distance effects) any given intensity of ionization between the maximum and the vanishing values may be maintained indefinitely by properly placing the radium tube; in the latter case (decay) all stages are passed through in 2 or 3 minutes. Beginning with dust-free non-energized air, the number of efficient nuclei decreases as the number of ions increases (for either or possibly both of the reasons already given) until the condensation takes place wholly on ions. For greater intensities of ionization the number of ions must increase further, and hence the efficient nucleation rises again while the curve passes through a minimum.

The curves enable us to make certain interesting comparisons, inasmuch as the same nucleation results from radium decaying for a stated length of time, as results from the action of radium at a certain distance from the line of sight. From the importance of secondary radiation in connection with these observations, such comparisons are probably not simple. The essential feature is the passage of the nucleation through the same stages of variation, whether of size or of number, in both cases no matter how the given successive intensities of ionization may be produced, or whether they come from within or without.

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* Considered relatively to the wide divergence after $t = 13$ sec. is passed. The coalescence need not be perfect. Small coronas fall out too rapidly for close measurement.

63. Decay curve.—Assuming that the rate of decay in the lapse of time (t) is as the square of the number, or that $1/n - 1/n' = b\ (t - t')$ where b is constant, a few incidental attempts were made to compute b.

Table 38 and fig. 48 contain an example of such results, obtained by exhausting the fog chamber at a stated time after the removal of radium. The drop in pressure is below the coronal fog limit of air and all precipitation takes place on ions.

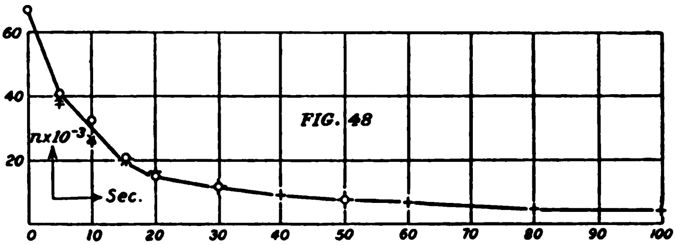

Fig. 48.—Decay of ionized nuclei (n per cubic centimeter) produced by radium in dust-free air, in the lapse of seconds. Table 38.

For the first five seconds $b = 0.0019$, for the first fifteen seconds $b = 0.0022$, etc., the values obtained ranging from 0.002 to 0.003. This is larger than the electrical datum 0.0014. Decay is more rapid than the equation warrants. Initial coronas are too large, final coronas too small, in spite of the presence of air nuclei, the number of which should be deducted at least in part. Other experiments show similar coefficients. Thus the low curve of Miss Joslin would conform to $b = 0.0023$. Naturally the present method for b is much inferior to the electrical method, even if the two coefficients are identical; but the b here is obtained under possible complications with the larger gradations of the colloidal nuclei of dust-free air, though these are probably inefficient.

Table 38.—Decay curve at $\delta p = 23$. Radium on top.

t.	s.	$n \times 10^{-3}$.	$n \times 10^{-3}$. $b = .0024$
sec.			
0	5.9	67	67.5
5	5.0	41	37.3
10	4.6	32	25.8
15	4.0	21	19.7
20	3.5	15	15.9
30	3.3	11.6	11.5
50	2.9	7.4	7.4
120	1.7	1.9	3.3
∞	1.0	1.1	....

If the values of $1/n$ be inserted, the curves should be linear, since $1/n = 1/n_0 + bt$, where t is the time dated since the occurrence of n_0. The line passing through the observations at 5, 30, 50 seconds is best adapted to represent the results, and compatibly therewith $b = 0.0024$ (n in thousands of nuclei per cubic centimeter) may be roughly assumed. These computed values of n are given in table 38 and shown in the chart (fig. 48). They are too low initially and too high finally, even if the air value is quite ignored; but the constant probably reproduces the true conditions better than the observation, remembering that the initial corona ($t = 0$) is not quite invariable.

A very important consequence may be deduced from these results. The equations specified may be written

$$\frac{1}{bt}\left(\frac{n_0}{n} - 1\right) = n_0.$$

Hence if the ratio of nucleations or of ions is known (for instance by the method of geometric sequences), n_0/n is given, and the absolute value of n may be computed if b is known. Now, if b, for the case of ions, may be taken as identical with the value found in electrical experiments, where $b = 0.0014$, roughly and relative to ionization in thousands, $bn_0 = 0.0014\ n'_0$ where n'_0 is the true nucleation. Thus in table 39, $b = 0.0024$, $n_0 = 67{,}500$; therefore $n'_0 = (0.0024/0.0014)\ n_0$ or 115,000 nuclei per cubic centimeter. Quite generally, if n_0/n and b are determined from purely coronal measurements $b/0.0014$ is the reduction factor for all the relative nucleations to absolute values.

Another very important consequence may be drawn. If the coefficient is known from direct experiments, it will then be possible to standardize the residual curve (depressed asymptote) leading to the terminal corona. Thus if $b = 0.0024$ is roughly assumed, as an example derived from the data at $\delta p = 24$ cm. (table 37 and fig. 47), the value of the ordinates of the curve for $\delta p = 31$ would then be given by table 39 and fig. 49.

Moreover, in any such curve, while the ordinates denote the computed number of ions, the abscissas denote the observed number of efficient colloidal nuclei and ions in the course of time, largely the former. Hence the curve gives an indication of the distribution of the precipitated water on the two groups of nuclei, different in size and present in different proportions, for the given supersaturation. Experiments of this kind are of the highest importance and the present cursory treatment is admitted provisionally, in view of a projected restandardization of the coronas of cloudy condensation, which the variety of results since obtained has made necessary. The curve for $b = 0.0024$ is shown in fig. 48; the two curves* i and $n+i$, i and n, in fig. 50. The initial descent of the graph for i and n is clearly steeper than would correspond to any exponential or hyperbola, and an equation of the form

$$i\ (n+A)^B = C$$

is at least needed to express the data. The computation of the constants would not be of any value. The table and chart show clearly enough how rapid a reduction of efficient nuclei is produced by the presence of but a few thousand ions. The results would have been much more striking if a more efficient form of apparatus had been used, since for $\delta p = 31$ cm. it is customary to obtain four or more times as many colloidal nuclei in the absence of ions.

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*Where i denotes the number of ions, n the number of nuclei per cubic centimeter.

TABLE 39.—Graduation of high pressure curve. $b = 0.002$; $n_0 = 75 \times 10^{-3}$; $1/n_0 = 0.0133 = a$.

t.	$n \times 10^{-3}$ at $\delta p = 31$.	$1/n_0 = A = 0.0133$; $b = 0.0024$.		
		$a + bt$.	$n \times 10^{-3}$.	$\{(n+i) - i\} \times 10^{-3} = n \times 10^{-3}$.
sec.				
10	*29	0.0373	†26.8	2
20	32	.0613	16.3	16
30	51	.0853	11.7	39
40	62	.1093	9.2	53
50	74	.1333	7.5	67
60	85	.1573	6.4	79
80	105	.2053	4.9	100
100	120	.2533	4.0	116
120	135	.3013	3.3	132
140	140	.3493	2.9	137
160	...	.3973	2.5	...
180	145	.4453	2.2	143
5	...	.0253^8	39.5	
15	...	.0493^8	20.3	

* $(i+n) \times 10^{-3}$. † $i \times 10^{-3}$.

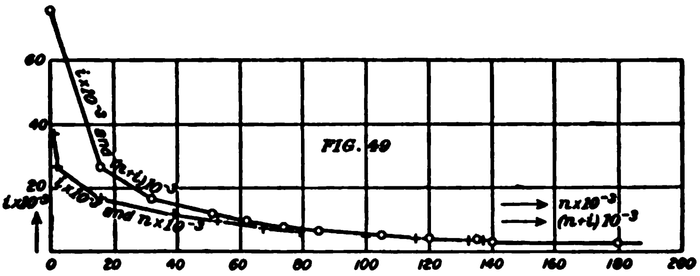

FIG. 49.—Decay of ions (i per cubic centimeter) in dust-free air, evidenced by increase of efficient colloidal nucleation (n per cubic centimeter). Table 39.

64. The same, continued.—In conclusion I may state that a number of experiments were made to test the rate at which the ions are generated. If a is the number of ions produced by the rays per cubic centimeter per second and b the coefficient of decay,

$$dn/dt = a - bn^2$$

This may be written

$$t = -\frac{1}{2\sqrt{b}}\int\frac{d\,(dn/dt)}{(dn/dt)\sqrt{a-dn/dt}}+C$$

from which, after integration,

$$\epsilon^{-2\sqrt{ab}\cdot t+c}=\frac{N-\sqrt{a/b}}{N+\sqrt{a/b}}$$

If

$$\frac{n-n_1}{n\times n_1}=A\epsilon^{-2bn_1t}$$

where A is a constant and $n_1=\sqrt{a/b}$,

$$n=n_1\frac{1+A\epsilon^{-2bn_1t}}{1-A\epsilon^{-2bn_1t}}$$

If $t=\infty$, $n=n_1$, $a=bn^2$, which is otherwise evident. The coefficient a is here taken as an absolute constant independent of n. In the preceding paragraph it was roughly assumed that $b=0.002$ if n is reckoned in thousands per cubic centimeter. Hence $a=0.000002\times n^2$. Thus if $n=10^3$, $a=2$ per cubic centimeter per second; if $n=10^6$, $a=2\times 10^6$, etc. Experiments were tried with the radium tube on a pendulum swinging above the fog chamber; also with the tube on an inclined plane moving rapidly across the chamber. But in both cases the results, which essentially require the opening of the stopcock of the fog chamber, are too involved to have any critical value, and they are therefore discarded here.

65. Condensation phenomena of the inclosed steam jet. Methods and results.—Some time ago (Bulletin No. 12, U. S. Weather Bureau, 1893), I obtained a series of results (shown for example in fig. 52) from observations of the behavior of the steam jet inclosed in a wide tube of thin sheet metal. The jet shown at j in fig. 50 plays into the tube AkA, about 2 inches wide and 2 or more feet long, the steam escaping at B. Sky-light L, from a mirror M, enters the tube axially, through a window a, and is observed through an opposite window, g. Room air enters at C, to cool the steam, and the temperature of the inflowing air is taken, as well as the pressure under which the steam escapes. Fig. 51 shows two such tubes arranged for differential work. These data are used in the construction of fig. 52, where air temperatures in degrees centigrade are horizontal and steam pressures in pounds vertical.

It will be seen that for each temperature of the inflowing air there is a definite steam pressure at which the field of the tube just becomes opaque, and condensation within the jet, therefore, begins to be tumultuous. The edge of the opaque field is sharply marked, and above 15 it is possible to pass through it in a march of continually increasing steam pressures; for the opaque field vanishes with a kind of cusp, dependent for its position, naturally, on the apparatus used.

What the figure imperfectly suggests, however, is the occurrence of similar loci of *axial color*, which run parallel to the edge of the opaque zone, on the clear side of it. The colors follow the spectrum series reversed, v, b, g, y, o, r, growing continually fainter and vanishing into daylight.

The field becomes at once opaque if a strong nucleator like phosphorus is placed near *C*, fig. 50; or any color may be obtained in this way by carefully regulating the additions of nuclei, as shown elsewhere. Mere smokes, like salammoniac, are ineffective; in fact the field made opaque by phosphorus may be cleared by such smoke, added in reasonable quantity.

Ordinary non-filtered air is practically ineffective.—This touches the first point to be made. I have shown elsewhere that the fog chamber and the steam jet mutually supplement each other; the former responding measurably to nuclei reckoned in thousands per cubic centimeter, the latter to nuclei reckoned in millions per cubic centimeter, to speak roughly. In other words, the whole sequence of coronas, of which there are many periods visible in an apparatus of reasonable size, has been passed through when the occurrence of axial color begins, the latter end with particles so fine as to be optically ineffective.

It is for this reason that ordinary non-filtered air, which produces such remarkable effects in the fog chamber, is almost without effect on the steam jet. A faint scarcely discernible pink tinge is all that is seen, and it is therefore possible to omit the filtration of air altogether. The use of dust-free air will not change the conditions, which lie wholly below the scope of the steam jet. This is even the case when the air is artificially dusted by less powerful nucleators like weak X-rays or weak radium, the additions being as a rule relatively insignificant.

As the increase of steam pressure can only increase the supersaturation, it follows that the tumultuous precipitation of the steam jet characterizing the opaque zone *must take place on the nuclei of dust-free air*, for at this stage of the phenomenon the corona-producing dusts are ineffective.

Much attention has been given by Professor Wood in this country, and by others abroad, to the occurrence of optical resonance in con-

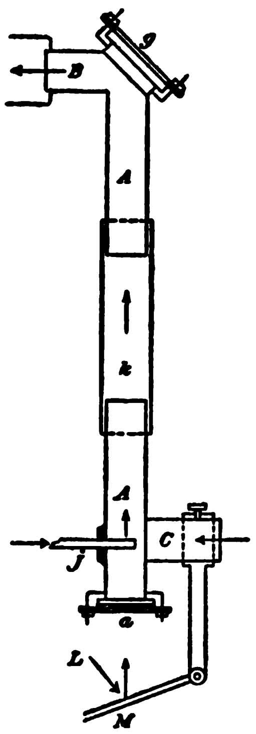

FIG. 50.

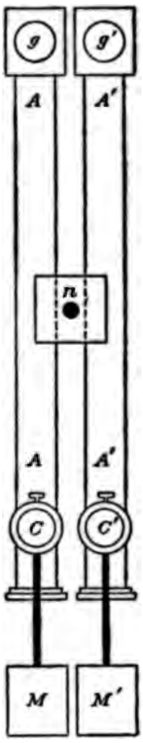

FIG. 51.

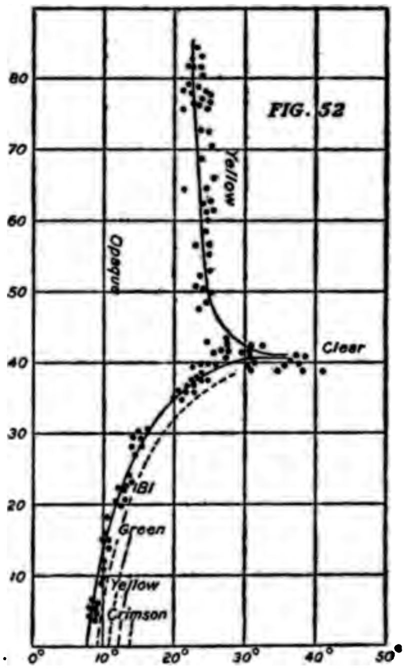

FIG. 52.

FIG. 50.—Section of inclosed steam jet and tube.
FIG. 51.—Binocular inclosed steam jet.
FIG. 52.—Chart showing margin of opaque zone for different steam pressures (pounds per square inch) and temperature of inflowing air.

nection with similar color effects. But the case of the steam jet may be duplicated, in different ways, by the vapors of typical non-ionizing liquids, like gasoline, benzol, carbon bisulphide, etc., with even more saturated axial colors than are observable in steam. Electrical resonance can not, therefore, be effective here, where the fog globules are dielectric. The particles, moreover, are too large to fall within the lines of such an explanation.

Returning to the diagram (fig. 52), it will be seen that at a temperature of about 40° there is no observable condensation; in other words, the steam passes through the tube like a gas, leaving the field quite clear. At 40°, therefore, the supersaturation at which condensation begins to take place on the nuclei of dust-free air is just reached; below it, at the given pressure, the supersaturation is in excess, and steam pressure must be relieved to reduce the excess before the field clears again, in greater measure as the temperature is lower, until at 9° steam issuing at ordinary pressure (without appreciable pressure above one atmosphere) condenses spontaneously.

The increments of supersaturation below 40° are in fact considerable. Thus, if the saturation at 40° be taken as the standard, these excesses would be roughly as shown in table 40.

TABLE 40.—Estimated supersaturations.

Temperature........	40°	35°	30°	25°	20°	15°	10°	
Supersaturation.....	0	12	21	28	34	38	42	$10^{-6}g/cm^3$.
Relation............	1	1.3	1.7	2.2	2.9	3.9	5.5	

These values are to be added to whatever supersaturation preexists at 40°, seeing that the escaping steam is always suddenly cooled down from a temperature much above 100°. In fact, the following data (table 41) may be adduced from the diagram, if t_1 be the temperature of the steam before, t_2 the temperature after, ρ_1 and ρ_2 the densities of the steam.

TABLE 41.—Estimated supersaturations.

t_2........	40°	35°	30°	25°	20°	15°	10°	
ρ_2........	50.9	39.3	30.1	22.8	17.2	12.8	9.3	$10^{-6}g/cm^3$
t_1........	112°	112°	112°	112°	111°	109°	105°	
ρ_1........	894	894	894	894	865	811	715	$10^{-6}g/cm^3$
$S=\rho_1/\rho_2$..	17.6	22.7	29.8	39.2	50.3	63.3	77	

Nothing more than exhibition of the order of values is intended; but it will readily be seen that in comparison with Wilson's data ($S=4.3$ for rain-like, $S=7.6$ for cloud-like condensation, and $S=9.9$ for the sensitive tint), the supersaturations here are enormous, and that the condensations must take place on something approaching the molecular groups of the system, water—steam—air.

It is therefore scarcely necessary to remark that the data are superior limits, particularly inasmuch as the influx temperature at *C*, fig. 50, and not the efflux *B*, were taken. But as the influx of air is swifter as the the steam pressure increases, the difference between these temperatures is not large. The escaping steam is always cool to the hand.

It follows that the color data bear at once on the structure of dust-free air. The occurrence of definite loci for r, y, g, b, v, the fact that any color can be retained indefinitely, if (*cæt. par.*) the pressure-temperature conditions are fixed, shows that groups of nuclei counted by millions per cubic centimeter must be available for condensation long before the molecular sizes are approached. It is convenient to refer to the molecular aggregates in question by the term "colloidal nuclei." They are necessarily much smaller than ions. The number of such nuclei increases as the supersaturation is greater and the size needed therefore smaller until condensation is actually spontaneous on the molecules themselves.

It is in this stage that one would naturally expect the fog particles of all sizes to produce a medium opaque to transmitted light, as is actually the case provided the fog particles are themselves large in comparison with the wave-length of light. It does not by any means follow, however, that the turbulent phenomenon is complete at the lower edge of the opaque zone. It is much more probable, seeing how gradually the violet drops into the opaque, as the supersaturations increase with increase of steam pressure at a given temperature of the inflowing air, that the number of nuclei continually increases. As this goes on (*i. e.*, in a vertical march through the opaque zone) the time must arrive when the fog particles become small in comparison with the wave-length of light; for although the influx of steam has increased, the air influx increases in the same proportion. Under these circumstances, even though fog particles of widely different sizes are the rule, the Rayleigh effect of scattering is to be looked for.

In fact, the yellows of the first order emerge from the opaque as magnificently saturated orange-browns and thereafter gradually become yellower. Deep crimson at the edge of the opaque does not appear. To prove that the passage from blue to yellow through opaque is due to an *increase* of nucleation, it is merely necessary to add phosphorus nuclei, when axial violet appears in the steam tube at a sufficiently high temperature. Without further change the bluish tone at once passes to yellow. Again, the intense oranges above the opaque may be obtained at once by introducing the fumes of the intensely nucleating sulphur flame into the steam tube. Finally, the probability of the Rayleigh effect is increased by the fact that colors of smaller wave-length than orange and yellow never occur above the opaque zone.

66. Summary.—The present chapter has made use of the method of testing the presence and number of relatively large nuclei by the depression produced in the terminal asymptote obtained when nucleation varies with the drop in pressure, or of the diminution in aperture of the terminal corona corresponding in a given apparatus to dust-free non-energized air. It was thus easily possible to trace the growth in number of the persistent nuclei produced by relatively intense X-radiation in the lapse of time, showing results similar to Chapter I, sections 14, 15.

In the same way the occurrence of water nuclei in the presence of colloidal nuclei or of ions was clearly exhibited. These are due to the evaporation of small fog particles, until the increase of vapor pressure due to surface curvature is balanced by the decreased vapor pressure due to some independent phenomenon. Hence if the exhaustions proceed with a slightly opened filter cock, such nuclei must be present in greater number as the evaporation is faster, because increasingly more particles evaporate than subside.

The result in the first place is a necessary alteration of aperture of successive coronas, all other conditions remaining the same, since the large ones evaporate more fog particles than those of lower order of size (periodicity of coronal diameter). In connection with this phenomenon it is particularly interesting to observe that not only the colloidal nuclei but the ions are available. Questions arise as to whether the fog particles of positive and of negative ions evaporate to like water nuclei, what becomes of the charges, since it is not clear that they should be dissipated, what phenomena arise from the decreased mobility of the loaded ions, etc.

The means developed in Chapter II were again applied to an effect produced (distance effect), when the radiating source is removed more and more from the fog chamber. The results are necessarily crude; but they show that in case of pervious wood fog chambers the nucleations decrease more slowly than the first power of distance; they decrease faster for the glass fog chamber; faster still when the X-ray bulb is inclosed in a windowed lead case; fastest when the window is closed with a thin tin plate; but in no case do they reach the law of inverse squares. All this points clearly to the importance of secondary radiation in producing nuclei. The radiation arises both near the bulb and near the fog chamber, as well as in the region between. The number of nuclei produced is therefore dependent upon an integral extended over the whole interior surface of the room and throughout the intervening air.

In case of exposure to weak radium (10 mg. 10,000×) the asymptote of dust-free air is not reached until the intervening distance is above 150 cm.; and it is far from appearing after 1.5 cm. of lead have been penetrated.

The occurrence of minima of nucleation, when such weak radium is carried from a long distance quite up to the fog chamber, is again strikingly brought out, provided the drop of pressure is sufficiently above the fog limit of dust-free air. It is also observed when the ions are produced in the fog chamber by radium and decay in the lapse of time after the radium is suddenly removed. The decay curves all show minima for a drop of pressure above the fog limits of dust-free air; while the curve is normal for pressure differences below the fog limit.

If the coefficient of decay for the ions within the fog chamber is the same as that found by purely electrical investigations, and if the relative numbers of nuclei corresponding in a given apparatus and given conditions of exhaustions are known, then a new method for the standardization of coronas in terms of the number of nuclei involved in their appearance, is suggested; for

$$n_0 = (n_0/n - 1)\ bt$$

if n_0 and n are two successive nucleations observed under like conditions at t seconds apart and if b is the known coefficient of decay. Conversely, if n_0 is given this method lends itself for the determination of nucleation ratios n_0/n, and for the experimental determination of the distribution of a given mass of precipitated water on groups of nuclei different in average size—one of the important of the outstanding problems.

Finally, it was shown that data bearing on the graded character of the colloidal nuclei of dust-free air may be obtained most directly and throughout the widest range from the behavior of the inclosed steam jet. If (*cæt. par.*) the steam pressure is intensified until the originally clear field (air dust being practically inactive), after passing a succession of colors, becomes clear again in consequence of absence of all condensation, it follows that colloidal nuclei in vast numbers and of continually decreasing size must successively become available for condensation until the fog particles are too small to be optically discernible. Each particular color corresponds to a group of colloidal nuclei characterized by their minimum size. It is still to be determined, however, whether these nuclei belong to the system of saturated vapor, or to the air, or to both.

CHAPTER IV.

DISTRIBUTION OF COLLOIDAL NUCLEI AND OF IONS IN MEDIA OTHER THAN AIR-WATER.

COLLOIDAL NUCLEI AND IONS IN WET DUST-FREE CARBON DIOXIDE AND IN WET COAL GAS.

67. Apparatus.—The following experiments were made with the apparatus used in my last experiments* with dust-free air. The conveyance tubes between the exhaustion chamber (5 feet long and 1 foot in diameter) and the condensation chamber (18 inches long and 5 inches in diameter) were about 18 inches long and 2 inches in diameter. The rapid exhaustion thus secured is effective, but has by no means reached a limit; there is still too much resistance in the connecting pipes. The data obtained with such an apparatus are comparable with each other, and nothing further than this is aimed at, since in view of the very high exhaustions needed, the constants for the computations of the absolute nucleations would in any case be lacking. It is a matter of convenience, however, to compute the data at the high exhaustion as if the conditions met with at the low exhaustion were indefinitely applicable, and this is the meaning to be given to n, the number of nuclei per cubic centimeter, in the present paper. Moreover, n refers to the nucleation left in the *exhausted* fog chamber, supposing that the nuclei are restored to the gas faster than they can be withdrawn by exhaustion or that the nucleation encountered is fixed for any definite environment. Otherwise n (to be multiplied by the volume expansion) would be very much larger.

The carbon dioxide used was generated from calc spar and hydrochloric acid. The gas was eventually passed through a solution of sodic hydrocarbonate, a long tube of dry bicarbonate of soda, a solution of silver nitrate, and a calcium chloride drying tube. Then it entered a filter (2 feet long), from which it was conveyed very slowly into the fog chamber. Coal gas taken from a gas pipe was treated in the same way.

68. Data for carbon dioxide.—In table 42, δp shows the drop of pressure on exhaustion, $s/30$ (approximately) the angular diameters of the coronas when the eye is at 30 cm. in front and the source of light 250 cm. behind the fog chamber. The meaning of the other data is obvious, n being the nucleation.

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*Phys. Review, XXIII, pp. 31-36, 1906.

TABLE 42.—Condensations in CO_2 generated from CaCo$_3$ with HCl. Gas washed as specified.

δp.	s.	Corona.	$n \times 10^{-3}$.
I. Washed in water, twice.			
31.0	(1)	g y o	410
31.0	10.7	w r g	260
31.0	7.8	w y g	140
31.0	6.4	w r g	100
31.0	5.3	cor	60
31.0	2.7	cor	8
31.0	2.4	cor	5
31.0	2.0	cor	2.9
19.1	2.1	cor	2.4
16.9	2.1	cor	2.2
II. Washed in solution of $NaHCO_3$ and $AgNO_3$.			
31.0	(1)	g y o	410
31.0	10.7	w o g	305
31.0	7.9	g|B P	150
31.0	3.3	cor	14.0
31.0	2.4	cor	5.0
31.0	[2]8.4	w r g	230
31.0	[2]11.4	w y b g	380
III. Same, with long tube of $NaHCO_3$.			
31.0	(1)	g y o	410
31.0	11.2	w o g	305
31.0	7.5	w B P	150
31.0	4.3	cor	32
31.0	4.4	cor	33
IV. Same, after 3 hours.			
31.0	[3]4 4	cor	33
17.6	1 ?	cor	1
17.1	0 ?	cor	1
17.7	1–2	cor	1
19.4	1 ?	cor	? 1
21.2	1–2	cor	1.5
24.7	1–2	cor	1.5
28.0	1.2	cor	1.5
31.0	2.0	cor	2.9
31.0	[4]9.6	w r g	240
V. Air bubbling through HCl, CO_2 off.			
31	12.0	w y b g	305
	12.0	w y b g	360
	....	[5]g y o	410
VI. Experiments with CO_2 repeated.			
31	(6)	g y o	410
31	11.0	w o bg	305
31	6.4	w r g	100
31	4.2	cor	29
31	[7]4.0	....	24
31	[8]4.2	....	29
31	2.1	cor	3.3
31	2.0	cor	2.9
35.1	10.0	w o g	320
40.3	...	green	500
31.4	1.8	cor	2.4
32.4	3.2	cor	12.9
33.5	6.7	g′ B P	140
34.7	9.8	w r o g	270
VII. Same.			
35.0	...	y o g	400
36.8	...	g	490
38.0	...	g B P	500
44.0	...	B g B P	550
VIII. Gas ionized. X-ray bulb at $D = 200$ cm.			
41.7	7.3	w y′ g	155
35.9	7.3	w o g	146
28.8	7.3	w o g	130
27.3	7.3	w o g	125
25.8	7.3	w o g	120
24.8	3.8	cor	20
23.3	2.5	cor	5.0
21.7	1.1	Just seen	1.2
24.2	4.2	cor	25
26.0	6.8	w r g	105
25.5	5.6	cor	62

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[1] s given for successive coronas beginning with air.

[2] CO_2 off; air inflowing.

[3] Not yet air-free.

[4] Exposure to X-rays.

[5] No trace of HCl gas escapes through the cleaning train.

[6] s given for successive coronas, beginning with air.

[7] After 1 hour.

[8] After 2 hours; other data consecutive.

In parts I to III in the table the exhaustion (δp) is usually kept constant, with the object of observing the behavior of the mixture of gases, beginning with air and terminating with CO_2. In part I about 8 exhaustions lead to the steady behavior of the latter gas. Inasmuch as the original air is still present to the extent of about 1 per cent, an admixture of this amount may be regarded as inappreciable. In the second part of the table, even four exhaustions, reducing the air content to about 11 per cent, nevertheless bring out the behavior of CO_2. The same things happen less certainly in part III. In part II, however, on readmitting air, two exhaustions nearly suffice to restore the air corona. Parts III and IV show that coronas for a given mixture are reproduced after several hours.

The relatively small coronas obtained with CO_2 as compared with air for the same drop in pressure and in the same apparatus gave rise to a suspicion that water nuclei associated with HCl gas might be involved. In part V, therefore, atmospheric air was bubbled through HCl and the gas then passed through the same drying train. After three exhaustions exceptionally high air coronas were obtained, showing that the method of producing the gas is of no consequence, thorough washing presupposed.

Hence, in parts VI and VII of the table, the experiments with non-energized CO_2 were concluded.

In part VIII of the table the gas is ionized by the X-rays with the bulb at a distance of 200 cm. The usual constancy of corona at high exhaustions is observed, while the fog limit is exceptionally high.

69. The behavior of carbon dioxide.—The graphs corresponding to table 42 are given in fig. 53, in connection with the corresponding data for air, both for the non-energized and energized states. It will be seen that in both cases the curves are essentially similar in their contours, but that the CO_2 curves require much higher exhaustion throughout than the air curves. In other words, the same coronas occur in CO_2 as in air, provided that in the former gas all the pressure differences are chosen to about 5 to 5½ cm. higher than in the case of air. Similar relations hold for the fog limits, as was found directly by Wilson* in a different apparatus.

The peculiar feature of these results is the degree of parallelism of the CO_2 and air lines, both for the non-energized and to a somewhat smaller extent for the energized state. Clearly the phenomena in both cases are alike in character, though lying far apart on the chart.

70. Cause of differences.—In view of the more coercible character of CO_2 one would naturally expect larger colloidal nuclei than in the case

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*C. T. R. Wilson: Phil. Trans. Royal Soc., vol. 189, p. 288, etc., 1897.

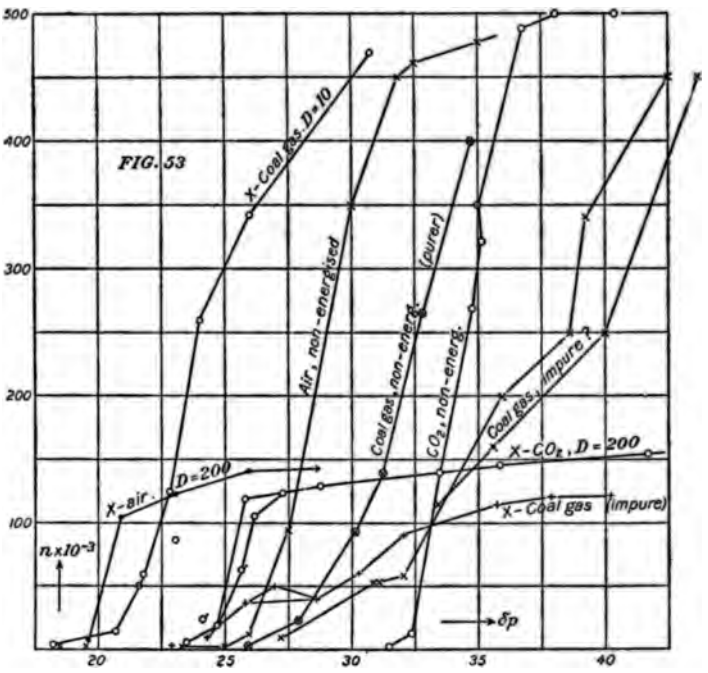

FIG. 53.—Efficient nucleation (n) observed in media water-air, water-CO_2, water-coal gas, energized or non-energized at different exhaustions δp.

of air, and it was with this anticipation that the data were investigated. Taken at their full value, however, they would point to a conclusion exactly the reverse of this. The colloidal nuclei in CO_2 are apparently smaller than in the air, and the same is true (*cæt. par.*) for the ions.

Unfortunately the precise meaning of these results is not clear, for in the first place the amount of adiabatic cooling may be written

$$\log \tau_0/\tau = (\gamma - 1)/\gamma . \log p_0/p$$

and thus between two fixed pressures

$$\log \frac{\tau}{\tau_0} = \text{const.} \frac{\gamma - 1}{\gamma}$$

The value of this fraction is for air, 0.29; for CO_2, 0.22; for coal gas, 0.19. In other words, the amount of cooling is less in CO_2 than in air under like conditions, and hence the reduced efficiency of the fog chamber in the former case is qualitatively compatible with the thermal properties of CO_2 gas. Quantitatively, however, this compensation does not seem to be sufficient. For instance, the same corona is obtained in air and CO_2 when the pressure difference is 28 cm. and 33.5 cm., respectively. For like nuclei this would imply the same degree of supersaturation. Hence, if p_1 and p_2 be the vapor pressures of water before (20° C.) and after exhaustion, and $p=76$ and $p-\delta p$ be the corresponding pressures, the occurrence of like supersaturation implies that

$$\frac{p_1}{p_2}\left(\frac{p-p_2-\delta p}{p-p_1}\right)^{\gamma}=\frac{p_1}{p_2}\left(\frac{p-p_2-\delta p'}{p-p_1}\right)^{\gamma'}$$

where p^1 and γ refer to CO_2 and where γ is the heat ratio for air. Hence

$$\frac{\gamma}{\gamma'}=\frac{\log\,(1-(\delta p'+p_2)/p)-\log\,(1-p_1/p)}{\log\,(1-(\delta p+p_2)/p)-\log\,(1-p_1/p)},$$

where the value for $\frac{\gamma}{\gamma'}=1.10$ as derived for direct experiment.

To compute the value of the same ratio from the coronal experiment it is necessary to know p_2 the vapor pressure on exhaustion and before condensation ensues. This datum is unavailable, but it must be greater than 0 and less than would correspond to the decidedly lower exhaustion $\delta p=17$ (for instance) than the one applied ($\delta p=28$). Hence limits of the value of $\frac{\gamma}{\gamma'}$ may be computed by inserting $p_2=0$ and $p_2=0.2$ respectively. The results are $\frac{\gamma}{\gamma'}=1.28$, both for the superior and inferior limits, as would be otherwise evident.

One may summarize these results as follows: Either the heat ratio of carbonic acid, γ', decreases in comparison with that of air, γ, very rapidly as temperature decreases, so that an average value of $\frac{\gamma}{\gamma'}=1.3$ instead of $\frac{\gamma}{\gamma'}=1.1$ is to be used in the preceding experiments; or the colloidal nuclei in wet CO_2, though distributed in a way closely recalling the case of air, are throughout smaller.

71. Nucleation increases subject to a uniform law of equilibrium.—The most interesting feature of the data for CO_2 is their repetition (under higher exhaustion) of the behavior of air. In other words, the two curves are closely parallel throughout their extent. This seems to imply that both are primarily dependent, not on supersaturation or cooling or on volume expansion, but on a common law of distribution of number with size of aggregates, such as is given by the theory of dissociation. In other words, a given drop of pressure of sufficient rapidity and from a specific initial value in each case generates the same number of colloidal nuclei, though it does not follow that the apparatus in all cases can entrap them. This is even true in different apparatus of different degrees of efficiency, as shown elsewhere.

One might perhaps suppose that cohesion of molecules is more frequent when collisions are less frequent or that effectively more large particles reside in the exhausted gas. There are other cases given below which seem to suggest this peculiar inference.

72. Data for coal gas.—These are given in table 43 in the same way as in table 42, both for the non-energized and for the energized gas when the X-ray bulb is at a distance of 200 cm. from the fog chamber. The measurements were much less satisfactory than the above, the corona being thin and blurred. This may perhaps be due to the fact that mixed gases are under examination.

TABLE 43.—Distributions of nuclei in coal gas, washed in water and $AgNO_3$.

	δp.	s.	Corona.	$n \times 10^{-3}$.		δp.	s.	Corona.	$n \times 10^{-3}$.
Coal gas	31.0	5.1	cor	55	Coal gas	17.6	.0	...	.0
	31.0	5.1	cor	55		19.9	1.7	cor	1.7
	31.0	5.6	cor	70					
	31.0	4.3	cor	30					
	33.4	6.7	w y g(?)	115	X-rays. $D = 200$ cm.				
	35.5	7.8	(Thin)	160					
	40.0	8.9	w P(?)	250					
	44.1	9.2	w y′	450	Coal gas	40.1	6.6	w o g	121
	42.1	10.2	w y	450		37.8	6.6	w o g	120
Same.	39.2	...	y o bg	340		35.7	6.6	w o g	115
	38.6	9.6	w b r	250		32.0	6.2	wrg	90
	35.8	7.7	w P	200		30.2	5.3	cor	60
	32.0	5.3	cor	60		28.6	4.7	cor	40
	27.3	3.1	cor	10		27.1	[1]5.2	cor	50
	25.8	3.0	cor	9		25.7	4.6	cor	35
	24.5	3.6	cor	16		24.3	3.4	cor	13
	23.2	2.2	cor	3		22.9	2.3	cor	3.5
	19.4	1.9	cor	2		21.7	1.5	cor	1.7
	18.4	1.3	cor	1		20.6	[1]2.3	cor	3.1
	15.7	.0	...	0		19.4	.0	cor	.0

[1] Fluctuation of s not infrequent.

73. Character of the early results for coal gas.—As in case of CO_2, the data for coal gas throughout lie in a region of relatively low pressure; *i. e.*, large drops in pressure are needed to produce the coronas. Fog limits are correspondingly high. This will again be qualitatively in keeping with the low heat ratio γ.

Apart from this, these first results with the hydrocarbon gas differ thoroughly from the character of the results for air and CO_2. In the non-energized gas the nucleations rise to the pressure difference at a rapidly accelerated rate, and this continues to the highest value which δp applied and long after the air and CO_2 nucleations have become stationary in the given apparatus.

Similarly for the energized gas the increase of nucleation is very gradual and the asymptote is scarcely reached within the interval $\delta p=$ 40 cm. of the experiment. All this is sharply in contrast with the rapidity with which air and CO_2 approach their respective asymptotes, as may be seen by inspection of the chart.

TABLE 44.—Coal gas energized by X-rays at $D=10$ cm. and in absence of rays. Two-inch pipes. Lead conveyance tubes.

δp.	s.	Corona.	$n\times 10^{-3}$.	δp.	s.	Corona.	$n\times 10^{-3}$.
32.9	(1)	Slate bl.	...	Bulb removed.			
30.8	(1)	g′G	470				
29.0	(1)	Grayish	...				
27.5	(1)	Grayish	...	19.4	.0	....	0.0
26.0	11	w y′	340	22.4	.0	....	.0
21.7	5.7	w r′	58	24.6	?.0	....	.0
20.6	3.5	cor	13	26.0	1.7	....	2.2
18.2	2.1	cor	2.3	27.9	3.8	....	21.5
16.9	.0	....	.0	30.1	6.4	w y	97
24.0	10.5	w y o	260	31.2	7.3	w be	137
22.7	7.8	g′B	125	32.8	9.5	w r o	270
21.5	5.4	w r	50	34.8	10.4	w y	400
				37.3	...	?w y′	410

[1] Coronas too vague for measurement.

74. New data for coal gas.—In case of the above results the large vacuum chamber was not quite filled with coal gas and there may have been diffusion from one vessel to the other. Again, the rubber connecting-tubes of the first experiment (though in advance of the filter) were replaced by lead connecting-tubes, as rubber is pervious to coal gas. Whether from these causes or others, the results came out quite differently after every part of the apparatus had been filled with coal gas. This is also shown in fig. 52 and the results themselves are inserted in table 44.

The new results for coal gas now conform in character with the data for media of air-water and carbon dioxide-water, and for the non-energized state, the coal-gas line lies between the curves for the other two media, as the figure shows. In like manner the curve for coal gas energized by the X-rays now betrays nothing abnormal. In endeavoring to discover reasons for the differences between the data of table 43 and table 44, the presence of rubber tubing in the former case comes nearest to suggesting a solution. Carbon disulphide emits nuclei spontaneously; whether these may pass through the filter has not been tested; but it is conceivable that the action of coal gas on vulcanized rubber may in a somewhat similar way to carbon disulphide be productive of nuclei.

If these are larger than colloidal nuclei, though they may still be much smaller than ions, they would pass through the filter and give rise to the very phenomenon of depression of asymptote observed in table 43.

75. Conclusion.—Neither from the cases of CO_2 nor of coal gas does it follow that coercible gases have larger colloidal nuclei than non-coercible gases like air. The apparent results are the reverse of this. If the increased difficulties of condensation in the former are due to smaller heat ratios (γ) as compared with air, there is no reason why CO_2, where γ is larger, should show greater condensation difficulties than coal gas where γ is smaller. The distributions of nuclei suggest a common law of dissociation or chemical equilibrium.

COLLOIDAL NUCLEI AND IONS IN DUST-FREE AIR SATURATED WITH ALCOHOL VAPOR.

76. Introductory.—In my report* on the solutional nucleus and elsewhere† I came to the conclusion that the differences in promoting condensation exhibited by positive and negative ions were more probably to be ascribed to the difference in chemical structure or composition involving a difference of size than to the electrical differences as such. Experiments made in Wilson's apparatus by Dr. Donnan‡ with vapors of methyl and ethyl alcohol, carbon tetrachloride, carbon disulphide, benzol, and chlorobenzol show that the supersaturation needed to produce condensation was not necessarily greater in ionizing than in non-ionizing solvents. With similar apparatus Dr. K. Przibram§ recently examined a series of alcohols and other bodies ionized by the X-rays, obtaining among a variety of data a noteworthy result with a direct bearing on the question here at issue. It appears that whereas in the case of water vapor the negative ions are more efficient condensation nuclei than the positive ions, the reverse holds for the alcoholic vapors. In cases of methyl, ethyl, amyl, and heptyl alcohols (including some other bodies like chloroform) the positive ions invariably require less supersaturation to precipitate condensation than the negative ions of the same body.

Interesting differences are therefore manifest in the behavior of vapors, and it seemed desirable to test the nucleation of a medium of ethyl alcohol and air in comparison with the media of water-air and water-carbon-dioxide hitherto examined. The former behaves in fact as if the nuclei were throughout larger than in the latter cases.

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* Structure of the Nucleus. Smithsonian Contrib., No. 1373, p. 161, 1903.

† Ions and Nuclei, Nature, LXIX, p. 103, 1903.

‡ F. G. Donnan: Phil. Mag. (6), III, pp. 305–310, 1902.

§ K. Przibram: Wien Sitzungsber., CXV, pt. IIa, pp. 1–6, 1906.

77. Apparatus and method.—The experiments were conducted with an apparatus in which the connecting pipes between the fog chamber (18 inches long, 5 inches in diameter) and the vacuum chamber (5 feet long, 1 foot in diameter) were 4 inches in diameter, containing a 4-inch counterpoised plug stopcock. The whole connecting system was about 22 inches long, one-half of it belonging to the fog chamber. Experiments made with water vapor, however, did not show any further marked advantage arising from the use of the large passage-way specified, over the former apparatus, in which the corresponding tube was 2 inches in diameter. It is therefore superfluous to adduce for comparison the new data for water vapor. The general method for work was that frequently described in connection with these investigations.

78. Properties of alcohol fog.—While the experiments of my preceding paper with the medium of water vapor and carbon dioxide gas showed unusually high values of the exhaustions needed to produce coronal condensation, the case of alcohol-air shows correspondingly low values of exhaustion as compared with those for water-air. The number of colloidal nuclei entrapped by alcohol vapor are about 3.5 times larger than is the case for water vapor under like conditions. Hence the coronas for alcohol are exceedingly dense by contrast. They are also much less pure in color, and particularly at high exhaustions become fog-like. The phenomenon is coarsened and measurement less satisfactory.

As the alcohol fog particles are larger in size, they subside more rapidly at the same exhaustion than water particles; but the occurrences are in the former case far from simple. While the corona (if not too large) remains nearly the same throughout the slow subsidence of water particles, the corona for alcohol particles decreases one-half or more in size during this period. In other words, the alcohol particles experience very rapid growth during subsidence, from which it follows that many of them must evaporate to compensate in part for the eight-fold or more enlargement in bulk of the survivors. The same fact may account for the blurred coronas; for the true initial corona being very evanescent is probably not seen. Conformably with this view it is impossible to exceed large white-reddish forms in the present apparatus and to reach the high greens observed with water vapor.

79. Number of particles.—In order to determine the number of particles corresponding to a given corona, it is first necessary to compute the amount of alcohol precipitated per cubic centimeter of the exhausted vessel by the sudden cooling incident upon exhaustion. This may be done by a straightforward approximation* with results shown in the following table, 45, where t_1 is the initial temperature of the saturated air within the fog chamber, t_2 the temperature after sudden exhaustion and before condensation, and t the temperature after the precipitation of the m grams of alcoholic fog per cubic centimeter. The drop in pressure is δp from $p=76$ cm. at 20° C. The data of the last column will be presently explained.

TABLE 45.—Precipitation of alcohol vapor at different exhaustions (δp), supersaturations (S), and radius (r), of nuclei.

δp.	t_1.	t_2.	t.	$m\times 10^6$.	$S=p_r/p_\infty$.	$r\times 10^7$.
cm.	°	°	°	*Grams.*		*cm.*
10	20	+ 3.2	+14.8	10.0	2.42	1.44
20	20	−15.3	+10.2	18.3	6.21	.75
30	20	−36.1	+ 3.2	22.8	21.4	.48
These may be compared with the case of water vapor.						
8.5	20	+ 5.8	+14.7	2.6	2.17	1.65
17	20	− 9.6	+ 8.8	4.6	5.68	.77
22	20	−18.9	+ 4.6	5.5	11.1	.58
30	20	−36.1	− 3.5	6.4	69.7	.35

We may infer from the table that in a perfect apparatus and for true pressure differences† water fog particles would reach freezing (0° C.) at $\delta p=24$ cm. and alcohol fog particles at $\delta p=34.5$ cm. Moreover, for the same corona there must be on the average about 3.5 times more particles in the alcoholic fog than in the water fog, which accounts for the opaqueness of the former.

For the reasons adduced it is not worth while to express the results otherwise than in round numbers, for the data involved are inevitably crude. The assumption of the law of adiabatic cooling as far as − 36° C. is questionable, in view of the admixture of saturated vapor; but as the densities of vapor are for alcohol about 8 per cent that of air and for water vapor about 7 per cent, this approximation in a rarefied atmosphere like the use of Boyle's law for a wet gas is probably admissible. It is different, however, with the latent heat of the vapor, which is required at the low temperatures, but is known (as a rule) only at temperatures near the boiling-point. From this and similar points of view, measurements of latent heat for the more common vapors at very low temperatures would be desirable.

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* C. T. R. Wilson: Phil. Trans., London, vol. 189, 1897, p. 300.

† δp computed as $p-p_2$ in the way shown in Chapter II, and not the apparent value observed at the fog chamber.

Finally, the point at which the drop in pressure ceases to be efficient, on account of the increasingly rapid inward radiation of heat from the vessel, is the most serious of the outstanding errors. I have endeavored to diminish it compatibly with the desideratum of a large and easily adjusted fog chamber by successively increasing the bore of the exhaust pipes and stopcocks; and this plan has been in the large measure successful. The extent to which the error is present, as the drop in pressure increases more and more, is nevertheless left unanswered. If the upper inflection of the distribution curve (fig. 56) is a criterion, *i.e.*, the occurrence of identical terminal coronas for successively increasing exhaustions, the fog chamber with water-air is efficient to about $\delta p = 31$ or 32 cm., with water and carbon dioxide to about $\delta p = 37$ cm., with alcohol and air to about $\delta p = 20$ cm. In the former case the vapor would be cooled from 20° to about $-10°$ C. even after condensation; in the latter case to about $+10°$. On general principles and in view of the low temperature of the water, it would seem probable that the efficiency of the fog chamber must vanish gradually. But the appearance of the curves is such as if the action were unimpaired up to a given terminal drop in pressure.

In every case the fog particles with the surrounding medium of vapor soon reach the temperature of the air again, so that additional moisture must arrive from somewhere. It is remarkable that the marked constancy of the water coronas in perfectly tight apparatus during this period gives no evidence of the evaporation; while the alcohol coronas decrease one-half in aperture or the preponderating fog particles actually grow. Even if this is compatible with the evaporation of the smaller particles, there is again no evidence for it. Much of the moisture must therefore come from the wet cloth and the water within the vessel, which are not cooled by the expansion.

80. Size of the nuclei.—Here it may be worth while to inquire into the reason why the precipitation in alcohol is apparently so much easier; or, what is the same thing, into the estimated size of the nucleus on which precipitation takes place in these several cases. The Kelvin equation as modified by Helmholtz* may be used for this purpose, as was done by the latter and by Wilson† in the form $p_r/p_\infty = \epsilon^{2T/Rs\vartheta r}$ where p_r and p_∞ are the vapor pressures at the convex areas of radius r and radius infinity, respectively, T the surface tension of the liquid of density (s), R the gas constant of its vapor at the absolute temperature (ϑ).

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*Helmholtz: Weid. Ann., XXVII, p. 524, 1886.

†Wilson: Phil. Trans., vol. 189, p. 305, 1897.

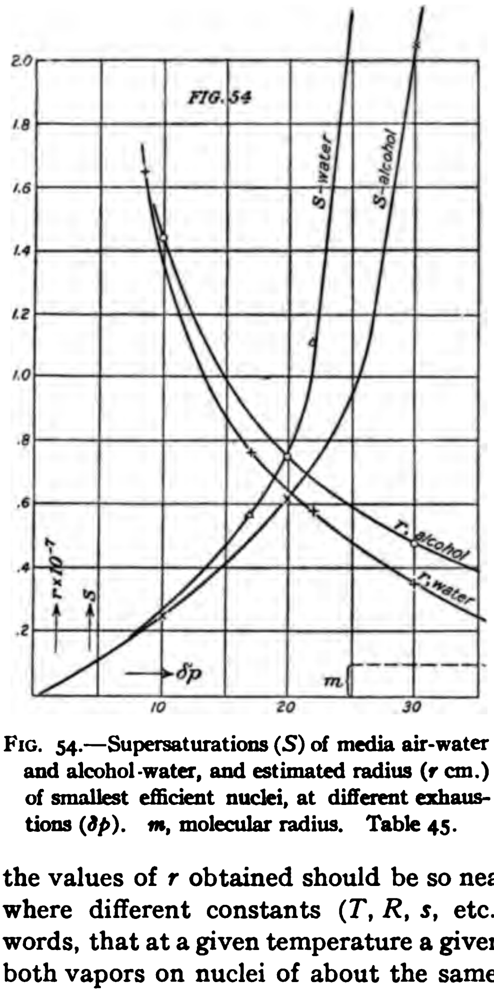

FIG. 54.—Supersaturations (S) of media air-water and alcohol-water, and estimated radius (r cm.) of smallest efficient nuclei, at different exhaustions (δp). m, molecular radius. Table 45.

Since p_r is the adiabatically reduced vapor pressure (without condensation) in the volume expansion due to the drop of pressure (δp) and p_∞ the normal vapor pressure at the same temperature ($\vartheta = 273^\circ + t_2$ in table 1), r follows from the equation. The values of p_r/p_∞ and r so found are both given in table 45, and have been constructed in the chart (fig. 54), where their relation to the usual order of molecular size is also indicated. Clearly these values of r, the radius of the nuclei differing so little from molecular radii (say 10^{-8}), can only indicate an order of values; for apart from the difficulties above enumerated in computing ϑ, r depends on surface tension (T), which has no meaning for molecular dimensions. Granting this, it is none the less remarkable that the values of r obtained should be so nearly alike for water and alcohol where different constants (T, R, s, etc.) occur throughout; in other words, that at a given temperature a given drop of pressure will condense both vapors on nuclei of about the same size.

In so far as these estimates are admissible it follows that the alcohol-air nucleus is larger than the water-air nucleus, since in the former case coronal condensation begins at about $\delta p = 15$ cm. where $r = 10^{-7}$ cm. and in water vapor it begins at $\delta p = 26$ cm. where $r = 4 \times 10^{-8}$ cm. about, less than half as large. These relations once established are retained through all successions of nuclei, as the following data for alcohol vapor in comparison with water vapor show. It is a little difficult to understand why the ionized nuclei in alcohol vapor should, like the colloidal nuclei, be larger than the corresponding cases for water vapor, unless the ions are aggregated vapor nuclei, a point of view tentatively advanced elsewhere; but this larger alcohol nucleus suggests that it is primarily

TABLE 46.—Colloidal nuclei and ions in alcohol vapor, energized or not; 4-inch cock.

	δp.	s.	Corona.	$n \times 10^{-3}$.
I. April 23. Not energized	30.8	10	[1]w r′	1,060
	28.4	10	[1]w r′	1,005
	26.0	10	[1]w r′	950
	23.0	11	[1]w y′	1,100
	21.1	10	[1]w c	615
	19.1	7.7	g B P	385
	17.3	4.8	cor	108
	16.0	2.4	cor	11
	4.7	1.5	cor	4
	13.4	1.1	cor	3
	12.3	(?)	([2])	0
	10.2	(?)	([2])	0
	19.9	(?)	([2])	0
	12.7	0	([2])	0
	16.7	5.0	cor	115
	18.5	7.7	g B P	380
	20.0	10.5	w r′	680
II. April 24	34.0	10	[1]w r′	940
	42.0	10	[1]w r′	1,040
	38.8	11	[3]w o′	1,170
	34.2	11	[1]w o′	1,110
	32.2	11	[1]w o′	1,080
	29.3	12	[1]w y′	1,270
	26.8	....	[1]w y′	1,210
	24.0	....	[1]w y′	1,120
	21.9	11	[1]w r′	720
	20.0	10	[1]w c	600
	18.3	8.2	w y	340
	16.7	3.5	cor	38
	15.0	1.0	cor	3
Later	14.8	1	cor	3
	16.3	5.0	[3]w r′	115
	18.3	7.6	w y b	320
	19.5	9.0	w r′	585
	21.7	10.5	w r′	720
	22.0	10.5	w r′	740
April 25	26.0	12	w y′	1,190
III. X-rays on. $D = 15$ cm	25.2	[4]12	w y′	1,160
	17.7	12	w y′	920
	15.1	11	w r′	650
	14.0	8.4	w y B	275
	12.9	2.6	cor	13
	11.5	.5	(?)	0
	11.5	.0	(?)	0
X-rays off	11.0	[5].0	....	0
IV. X-rays on. $D = 15$ cm	12.4	[5].0	....	0
	13.2	5.1	cor	101
	14.2	8.1	w B P	275
	15.1	10.	w r′	490
	16.1	10.5	w r′	580
April 26	36.6	11	w y′	1,420

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[1] Accompanied by dense fogs, rapidly subsiding, with coronas dwindling.

[2] Small coronas probably due to shaking.

[3] All coronas accompanied by dense fogs.

[4] Coronas decreased in size during subsidence, more than one-half.

[5] Coronas often due to solutional nuclei; produced by shaking.

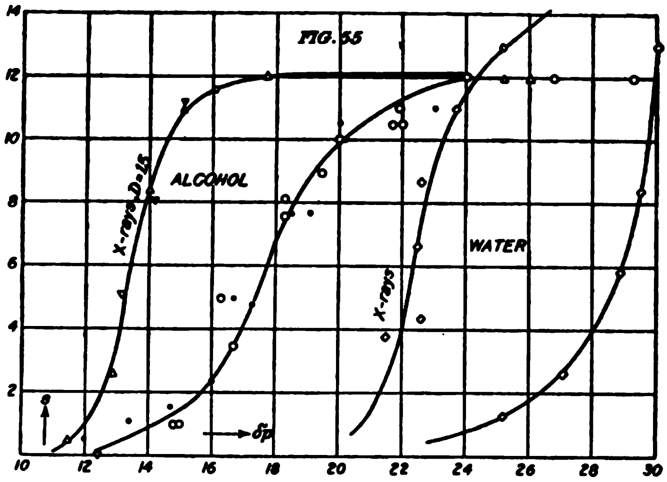

Fig. 55.—Aperture of coronas (s), observed at different exhaustions (δp), in media of alcohol-air, water-air, energized or non-energized. Table 46.

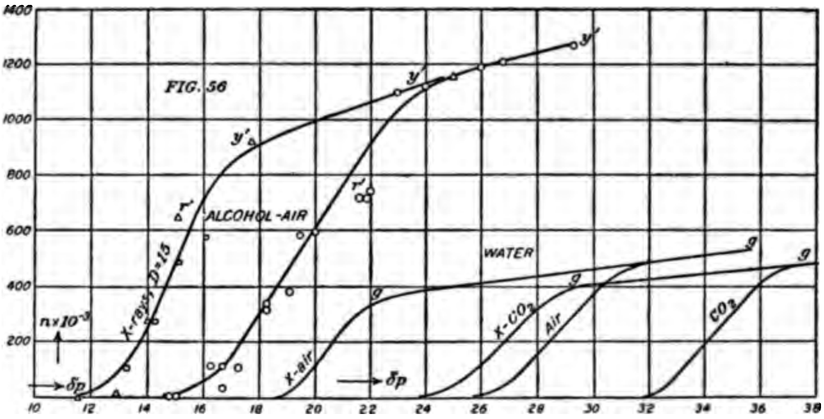

Fig. 56.—Efficient nucleation n in energized or non-energized media of alcohol-air and water-air, at different exhaustions (δp). Table 46.

the saturated vapor which furnishes the colloidal nuclei and that the gas is only secondarily involved.

81. Data for alcohol vapor.—The behavior of alcohol vapor is shown in the usual way in table 46, where δp is the sudden fall in pressure from atmospheric pressure producing the corona of the angular diameter $s/30$, when the eye and the source of light are at distances 40 and 250 cm. on the opposed sides of the fog chamber. The nucleation n is computed in the way given above, section 79, and indicates the number of nuclei in the *exhausted* fog chamber. It is assumed, therefore, that the nuclei are reproduced more quickly than they can be withdrawn by the exhaustion. Measurement of s is not very satisfactory, as the coronas are blurred and accompanied by dense fogs and changes rapidly on subsidence. The effect of X-radiation is shown in parts III and IV of the table leading to the same terminal corona as for the non-energized vapor.

The results have been given graphically in figs. 55 and 56, the former referring to coronas (s), the latter to nuclei (n), in connection with earlier results for media of water-air and water-carbon dioxide, the same condensation apparatus and method underlying all experiments. One may notice at once that in the cases CO_2-water and air-water, both for the non-energized and for the energized state, the observed data would be obtained by shifting the air-water diagram as a whole to the right, as if the cooling in case of CO_2-water vapor were less efficient. The graphs are of the same kind, nearly parallel, and all of them (energized or not) terminate in the same asymptote or large green-blue-purple corona.

The alcohol curves are different from these chiefly in three respects: (1) Though the graphs both for the non-energized and energized states again terminate in the same asymptote, this is not the green-blue-purple corona, but the white-yellow corona which lies slightly below it; (2) the curves as a whole lie with a somewhat larger slope in a region of much lower exhaustions (δp); (3) the number of nuclei caught in alcohol vapor is relatively very large. The second and third observations have already been discussed. The first deserves especial consideration. The question occurs at once why both the energized and the non-energized curves should terminate in the same final corona, irrespective of the size of the nuclei, and why this should be lower for alcohol than for water. For the ionized state one might infer that the total number of ions has been precipitated, as is actually the case for low ionization; but if for strong ionization this were true for alcohol vapor it could not be true for water vapor where the number of ions caught is less than one-half the number in alcohol. In general, it is improbable that the terminal corona for ions should in such a case be the same as the terminal corona for colloidal nuclei.

The explanation which seems plausible to me is this: Each nucleus must drain the air of its supersaturated moisture within a certain radius, large as compared with the size of the nucleus and increasing in the lapse of time.

A limit of the phenomenon will be reached when for an indefinite number of graded nuclei the enveloping spheres free from supersaturation form a system in contact. In case of water vapor the distance between centers would be 0.014 cm.; in case of alcohol 0.010 cm., distances which are both enormous as compared with the estimated size of nuclei (*r*, table 45, fig. 54). The greater distance which belongs to water vapor would be in keeping with its greater diffusivity, though this surmise does not work out for water-carbon dioxide as compared with water-air. At all events, when the limiting number of nuclei has been captured, the apparatus is powerless to produce condensation on a greater number of nuclei, be they relatively large as the ions or small as the colloidal nuclei, however many other inefficient nuclei may be present.

ABSENCE OF COLLOIDAL NUCLEI IN STRONG ODORS.

82. Introductory.—Throughout the course of my work I have been endeavoring to find whether bodies with strong odors and presumably large molecules could be regarded as a source of colloidal nuclei; or whether there is any relation between the colloidal nucleus and the odors. In case of carbon disulphide, from which nuclei apparently escape spontaneously, this would seem to be the case; but it is yet to be proved that vapor of carbon disulphide, if carefully filtered, nevertheless still produces colloidal nuclei in the fog chamber. In the present instance it is not improbable, if relatively few CS_2 molecules are oxidized SO_3, that sulphuric acid nuclei are the result. The experiment which has already been discussed is well worth while; but I did not make it, in the fear of contaminating the vacuum chamber. The following experiments show, however, that even in the extreme cases odors are due to molecules, and that in relation to the fog chamber, apparently large molecules are still quite negligibly small in comparison with the colloidal nuclei.

83. Data for camphor, turpentine, naphthalene.—The results obtained are given in table 47 in the usual way. The glass fog chamber was provided with a hole in the (thick) bottom, about 2 cm. in diameter and closed with a rubber cork. It was free from leakage from without. The bodies to be examined were introduced through the hole in question, and suspended in the middle of the fog chamber by aid of a wire-gauze tube 20 cm. long and 2 cm. in diameter. After putting this tube in place the air was carefully cleansed by precipitation of dust.

On May 5, 6, and 7, after putting the apparatus together, the medium within was first examined without introducing the odoriferous body. The internal sources of spurious nucleation gradually vanish. The

TABLE 47.—Miscellaneous experiments. Water nuclei effect of metal surfaces, of odors, etc. $\delta p = p - p_2$. Four-inch pipes and plug cock.

Date, etc.	δp.	s.	Corona.	$n \times 10^{-3}$.
May 5. Wet cloth lining in exhaust tube..	30.8	9.4	w r g′	240
	30.6	[1]6.5	cor	105
	30.8	10.0	w r g′	260
May 6...............................	30.8	12.0	wy bg	380
May 6...............................	30.8	[1]11.0	w r g	275
	30.8	11.0	w r g	275
	30.5	10.0	w p g	230
May 7...............................	30.6	11.0	w y′ g	380
Examination of odors:[2]				
May 8. Air only..................	30.7	11	w r g	305
	30.6	11	w r g	275
May 9. Air, camphor in............	30.8	11	w o g	305
	30.8	11	w y g	380
May 10. Camphor...............	30.8	13	g′ to gy	410
	30.8	13	g′	455
May 11. Camphor...............	30.8	13	g′ to gy	425
Air without camphor...........	30.6	13	g′ to gy	425
May 12. Air....................	30.6	12	y o	410
May 13. Turpentine.............	30.7	(3)	g y o	410
May 15. Naphthalene[4]............	30.6	13	g to gy	425
	30.6	13	g B P	455
	30.8	13	g B P	455

[1] Foreign nuclei not absent in second exhaustion.

[2] Hole drilled in bottom of glass fog chamber, closed by rubber cork.

[3] Apparatus blurred.

[4] Enlargement of coronas due to second (smaller) exhaustions.

exhaust pipes were cloth-lined and the cloth kept wet to guard against minor saturation error. On May 8, with the introduction of camphor, the nucleation apparently rises to a maximum (g-b-p. corona); but the same result is maintained after the removal of the camphor and the gauze (tested in many observations not recorded in the tables). Hence the camphor nuclei can not be larger than the colloidal nuclei of air-water; for the presence or absence of camphor within a fog chamber is inappreciable. The same conclusion follows from the experiments with turpentine (where the walls of the fog chamber were speedily blurred from distillation of small quantities out of the lamp wick holding the liquid) and from naphthalene. It is fair to conclude that presumably large molecules are nevertheless bodies of an inferior order of size relative to the colloidal nuclei of dust-free air.

84. Summary.—Media of coal gas and water require higher exhaustion than media of air and water, media of carbon dioxide and water higher than coal gas and water, to precipitate condensation in like degree, other things being equal. On the other hand, media of alcohol and water require smaller exhaustion to precipitate an alcohol fog in corresponding degree. The general character of the phenomena in all these several cases are, however, the same. Their relation to each other when the media are energized in like manner by the X-rays is also the same. (*Cf.* fig. 56.)

It does not follow, therefore, that wet coercible gases like carbon dioxide and coal gas contain larger colloidal nuclei than wet air. The apparent result would be quite the reverse of this. Neither can the difference be explained in terms of the respective value of the ratio of specific heats (γ); for in relation to condensation, the order is air, coal gas, carbon dioxide; in relation to γ, air, carbon dioxide, coal gas. The probable occurrence of large colloidal nuclei in media of alcohol and air and relatively small colloidal nuclei in water and air seems to show that the colloidal nuclei are primarily to be associated with the saturated vapor, and that the gas involved is of secondary importance. It can not be a question of mere solubility of gas in the vapor, for this is strongest in water and carbon dioxide, in which there is no evidence of large nuclei. The curves of distribution of number with size are again such as to suggest a common law of equilibrium.

The presence of strong odors (camphor, naphthalene, turpentine, etc.) in the fog chamber is without an appreciable effect. Hence the colloidal nuclei can not be large molecules merely, and colloidal nuclei can not be ascribed to chemical impurities in the gas.

Continued slow exhaustion seems to be favorable to the growth of fog particles and the formation of rain.

Both for the energized and for the non-energized state, the graphs for the same media, though referring to nuclei of widely differing sizes (ions, colloidal nuclei), again terminate in the same asymptote, or end in the same terminal corona. This is not identical for different media, however, the corona being of lower order though denser for alcohol and air, of higher order but thinner for water and air, for instance. The number of nuclei caught (*cæt. par*) in alcohol and air is much larger than in water and air. When the limiting number of nuclei has been reached by condensation, the system is powerless (in a given apparatus) to condense on a greater number of nuclei, be they relatively large like the ions or small like the colloidal nuclei.

CHAPTER V.

THE COTEMPORANEOUS VARIATIONS OF THE NUCLEATION AND THE IONIZATION OF THE ATMOSPHERE OF PROVIDENCE.

BY LULU B. JOSLIN.

85. Introduction.—The results obtained by Professor Barus,* showing a characteristic succession of the values of atmospheric nucleation throughout the year, suggested a parallel inquiry into the variations of the number of ions in the atmosphere in the lapse of time. The present work was therefore undertaken at his instigation, and observations systematically carried forward from August, 1905, to April, 1906.

In addition to the main purpose in view, it was hoped that a number of subsidiary questions might be answerable. Thus a large part of the nucleation of Providence is of local origin and enters the atmosphere with other products of combustion. Initially these nuclei were either highly ionized themselves, or at least the atmosphere originally received an accession of ions and nuclei in proportional quantities. It is therefore of interest to inquire whether any of the ionization survives, or whether there is any connection observable between corresponding changes of the nucleation and the ionization of a given place. The results, which are carefully tabulated in the present paper, seem to show that there is no such connection whatever; or that the persistent ionization arises from, and is maintained by, causes which are quite distinct from the nucleation. No evidence has been found to suggest that the ionization is either emitted or absorbed by the nucleation, whence it follows that the ionization arises from causes wholly non-local. Apart from these main purposes, the data are interesting as a continuous record of ionization (which will be supplemented in the future), though, as yet, sufficient time has not elapsed to ascertain whether the opposition in the monthly positive and negative ionizations found in the sequel is real or incidental. (*Cf.* fig. 62.)

Finally, I may add that work to investigate a possible relation between the nucleation and the ionization of the atmosphere was undertaken in Helgoland and on the coast of the Ostsee by Prof. G. Lüdeling† in 1902 and 1903, using Aitken's dust-counter. The time during which observations were recorded (August 21 to September 16, 1902, June 17 to July 4, 1903) were insufficient to warrant general conclusions, however, apart from the interesting special investigations which Professor Lüde-

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* Smithsonian Contrib., XXXIV, No. 1625, chap. IX, 1906; Carnegie Institution publication No. 40, January, 1906, chaps. IV and V.

† Two papers in the Veröffentl. Königlich Preussischen Meteorologischen Instituts, Berlin, 1904.

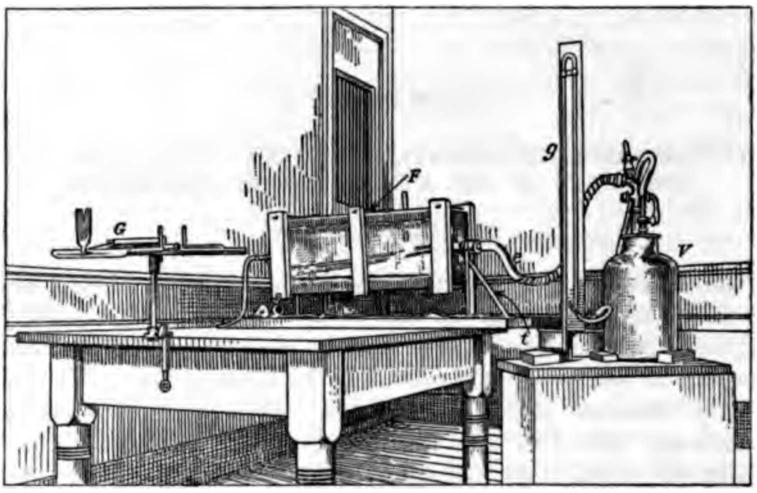

FIG. 57*a*.—Disposition of coronal apparatus for measuring atmospheric nucleation ("dust"). *V*, vacuum chamber; *F*, fog chamber; *G*, goniometer; *g*, gage; *e*, exhaustion pipe; *t*, support for trunnions. Influx pipe at left end of fog chamber.

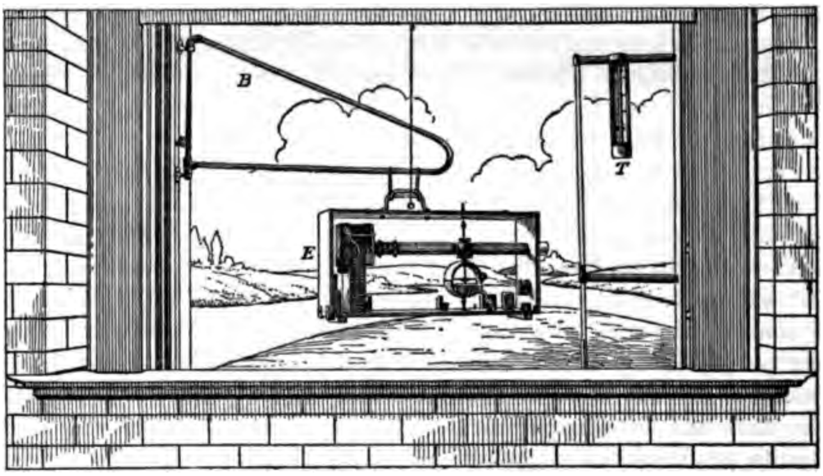

FIG. 57*b*.—Disposition of apparatus for measuring atmospheric ionization. *E*, Ebert's apparatus; *B*, swiveled brackets sustaining the same; *T*, thermometers.

ling's paper contains. Reference should also be made to P. Langevin's* important discovery of slow-moving ions in the atmosphere and to the work of M. Bloch,† but comparisons of this nature are quite beyond the scope of the present straightforward experimental research.

86. Measurements of nucleation.—Number of nuclei in the atmosphere were measured by aid of the corona of cloudy condensation, in the way fully described by Professor Barus (*loc. cit.*, chap. 8), and the same apparatus (fig. 57*a*) which had proved efficient in the earlier investigations was used throughout the present experiments. *F* is the revoluble wood fog chamber with plate-glass windows, *V* the vacuum chamber, *i* the influx, *e* the exhaustion pipe, *g* the gage, *G* the goniometer. Source of light beyond *F* is not shown. Two or more observations were usually made daily, together with the meteorological elements of wind, weather, and similar data. The ionizations referred to below, section 91, were taken in the same place.

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* P. Langevin: Bull. Soc. Franç. de Phys., p. 79, 1905.

† Bloch: "Recherches sur la conductibilité électrique, etc.," Paris, 1904. See C. T. R. Wilson, Trans. Intern. Congress, St. Louis, vol. 1, p. 365.

87. Data for nucleation.—In table 48 the first column shows the day and month, the second the time in hours and tenths of an hour. The third gives the current weather, F denoting fair, F′ partly fair, C′ partly cloudy, C cloudy, R rain, Sn snow, etc. The temperature of the fog chamber. (°C.) and the temperature of the atmosphere (°F.) follow. The remaining columns show the data referring to the coronas, the sixth giving the diameters (*s*) of the coronas at the end of a radius of 30 cm. Hence $s/30$ is nearly their angular diameter when the eye and the source of light are at distances 85 cm. and 250 cm. on opposite sides of the fog chamber. The seventh column indicates the colors of the successive annuli of the coronas, reckoned from within outward, w denoting white, r red, o orange, y yellow, g green, b blue, p purple, etc. A vertical line (|) shows an indeterminable color, a prime (′) an approach to a color, etc. The last column gives the number of nuclei in thousands per cubic centimeter, deduced from the amount of water precipitated per cubic centimeter, and the sizes of particles in successive coronas, as listed by Professor Barus (*loc. cit.*).

88. Remarks on the table of nucleation.—With regard to the individual observations very little can be adduced that has not already appeared in the earlier work. Conformably with the mild winter, the nucleation as a whole is relatively low, an unfortunate occurrence in its bearing on the purposes of the present work; but deductions of this character will be brought forward with advantage in connection with the daily and monthly mean nucleations below. It is rather curious that the forest fires on Cape Cod in the early May and the powder combustion on July 4 produce so little impression; on the other hand, the cold weather in August is at once marked by large coronas.

89. Mean daily nucleation.—The data of table 48 have been averaged for the successive days in table 49, with other data at once intelligible. The results, if given graphically with the current days as abscissas, the corresponding mean nucleations in thousands per cubic centimeter as ordinates, show no new points of view. One may note the rare occurrence of the large g-b-p coronas so frequently met in the high nucleations of the preceding winter.

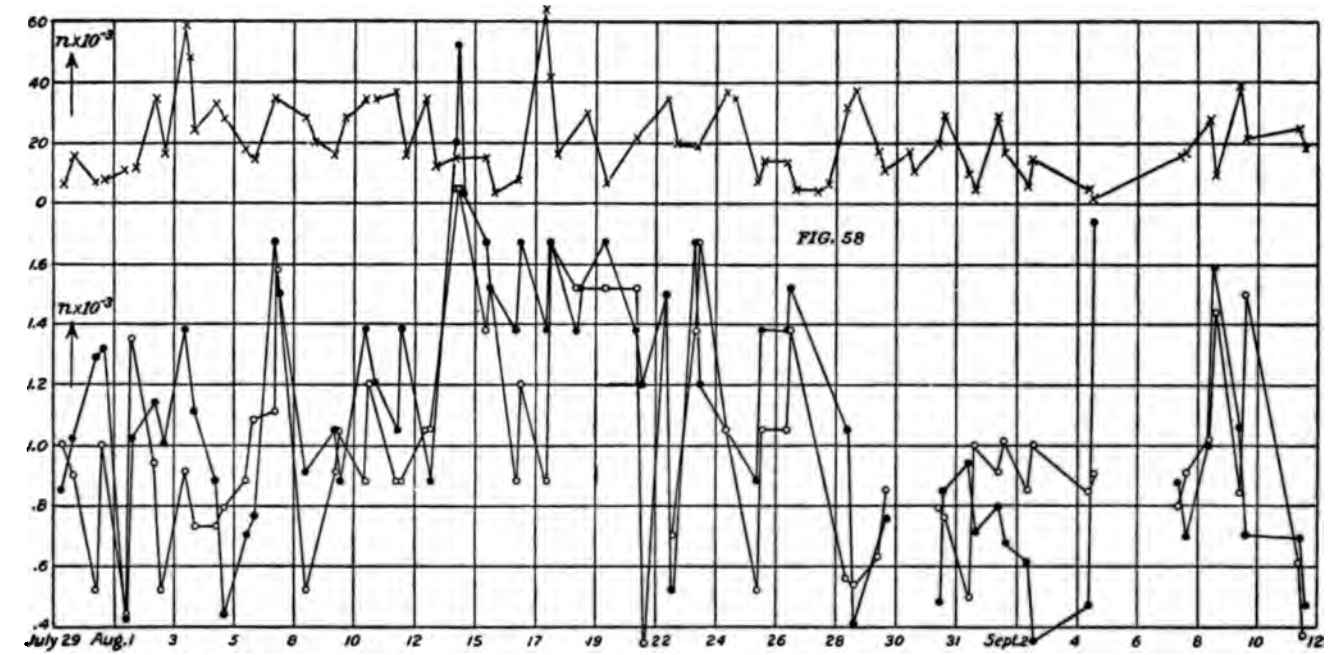

FIG. 58.—*Lower curves:* Daily ionization (*i*, thousands of ions per cubic centimeter) at the times given from August, 1905, to March, 1906. Positive values marked by open, negative by black circles. Observations connected by straight lines. *Upper curve:* Daily nucleations (*n*, in thousands of nuclei per cubic centimeter) observed at the same time. Table 49.

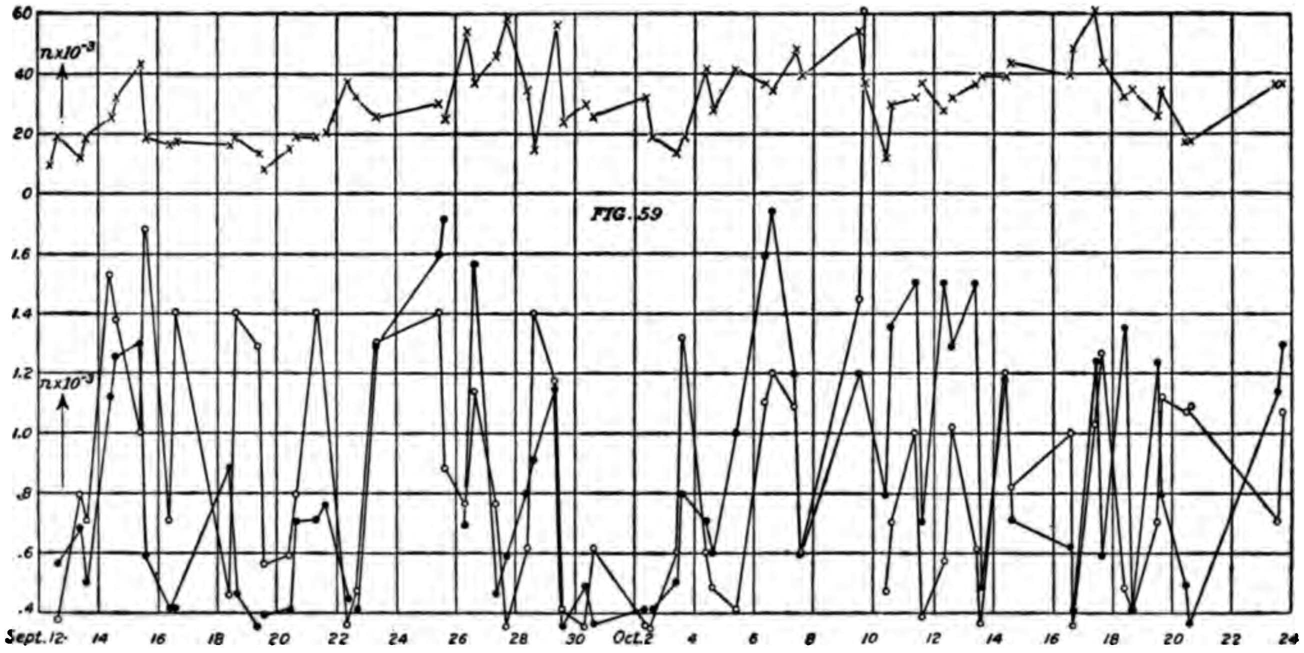

FIG. 59.—*Lower curves:* Daily ionization (*i*, thousands of ions per cubic centimeter) at the times given from August, 1905, to March, 1906. Positive values marked by open, negative by black circles. Observations connected by straight lines. *Upper curve:* Daily nucleations (*n*, in thousands of nuclei per cubic centimeter) observed at the same time. Table 49.

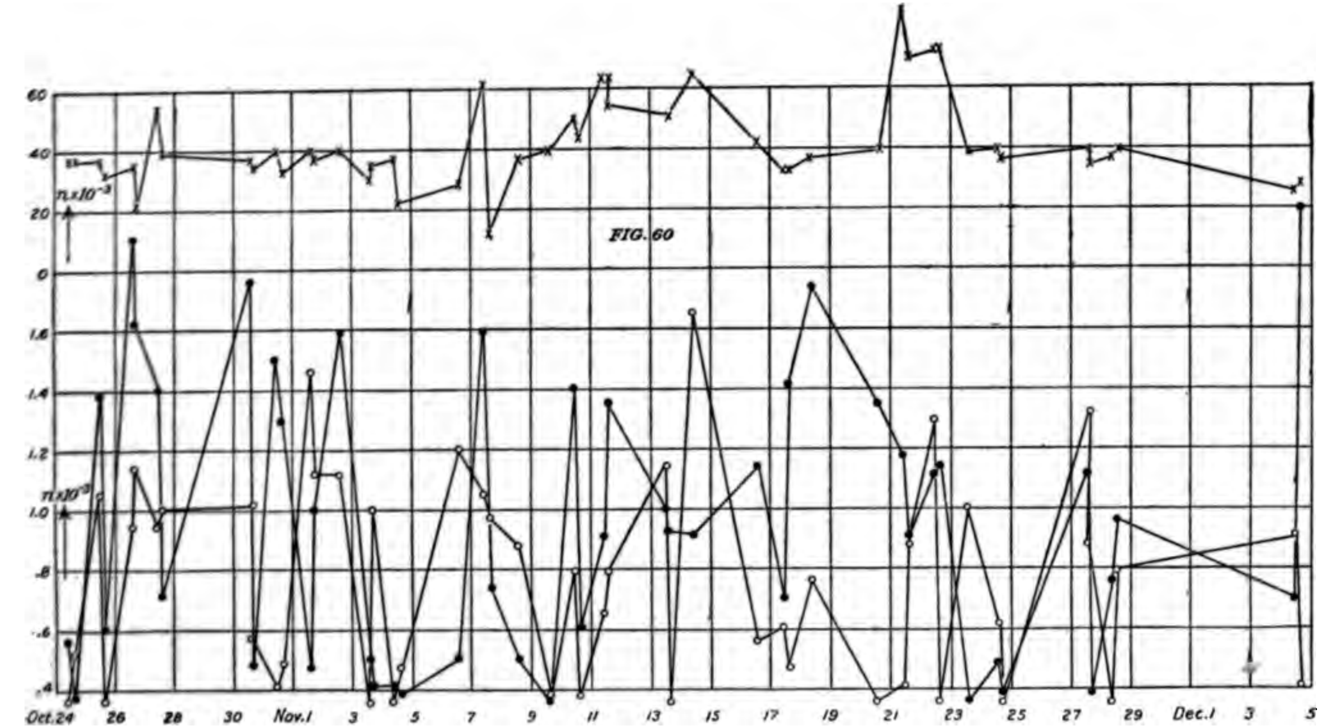

FIG. 60.—*Lower curves:* Daily ionization (*i*, thousands of ions per cubic centimeter) at the times given from August, 1905, to March, 1906. Positive values marked by open, negative by black circles. Observations connected by straight lines. *Upper curve:* Daily nucleations (*n*, in thousands of nuclei per cubic centimeter) observed at the same time. Table 49.

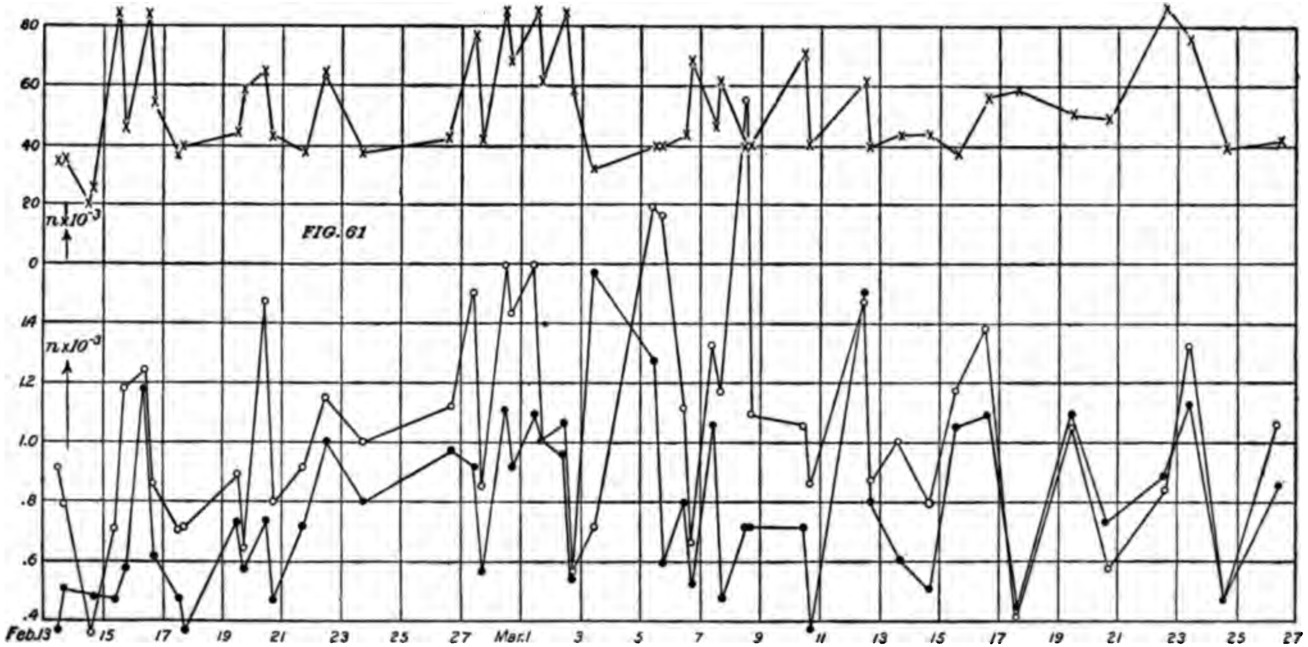

FIG. 61.—*Lower curves:* Daily ionization (*i*, thousands of ions per cubic centimeter) at the times given from August, 1905, to March, 1906. Positive values marked by open, negative by black circles. Observations connected by straight lines. *Upper curve:* Daily nucleations (*n*, in thousands of nuclei per cubic centimeter) observed at the same time. Table 49.

TABLE 48.—Showing the number of nuclei, n, per cub. cm., in the atmosphere at the times (in days and hours) stated. The temperature given in degrees F. refers to the atmosphere, the temperature in degrees C. to the fog chamber.

Date.	Time.	Weather.	°C.	°F.	s.	Corona.	$n \times 10^{-3}$.
1905.	*Hours.*						
May 4	9.8	C	21	50	3.2	cor	11.3
	12.7	C	21	53	3.2	cor	11.3
	6.2	F	21	53	3.2	cor	11.3
5	9.4	F	20	57	4.9	w B P	41.7
	6.0	F	20	54	4.6	cor	34.8
6	9.6	F	20	68	5.9	w C g	68
	12.7	C	21	75	6.6	w o g	90
	1.1	..	..	..	5.8	w P cor	64.5
	6.0	C	21	68	4.9	w o g	41.7
7	9.7	C′	21	75	4.8	w o g	39.5
	1.5	C′	21	84	4.8	w o g	39.5
	6.8	F	22	73	3.8	cor	19
8	9.0	F	21	60	6.7	w o g	92.5
	9.5	F	21	65	7.1	w y g	100
	3.0	F	21	65	4.8	w r g	39.5
9	9.8	R	20	61	4.8	w r g	39.5
	1.4	F	21	65	4.9	w B P	41.7
	6.3	F	20	59	4.6	w o g	34.8
10	9.6	F	19	60	5.6	w o g	58.7
	3.3	F	19	68	4.7	w o g	37.2
	6.2	F	..	66	4.7	...	37.2
11	9.3	F	19	66	5.6	w c g	58.7
	6.2	F	20	65	4.5	w r g	32.4
12	3.2	C′	20	68	3.8	cor	19
	6.0	C′	..	66	4.7	...	37.2
13	9.4	C′	..	60	4.6	...	34.8
	2.8	C	18	62	3.6	cor	16.2
	6.3	C	..	55	3.2	cor	11.3
14	9.8	C	19	59	3.3	cor	12.5
	1.4	R	19	49	3.8	cor	19
	6.2	R′	19	61	3.8	cor	19
15	9.1	C	19	60	4.5	w r g	32.4
	3.8	C′	19	67	3.6	w r g	16.2
	6.3	C	19	61	3.6	w r g	16.2
16	9.3	C	18	55	3.5	w r g	15
	3.4	R′	18	52	3.1	w r g	10.2
17	9.3	C	18	49	3.6	cor	16.2
	6.0	C	17	49	3.9	cor	20.5
18	9.4	C	16	55	3.7	cor	17.5
	2.8	F	18	65	4.6	g B P	34.8
	5.0	F	18	64	...	...	....
19	10.0	C′	18	65	4.5	w r g	32.4
	6.0	C′	18	66	4.6	w r g	34.8
20	10.3	F	17	57	6.0	w c g	70.5
	6.3	F	18	58	3.9	cor	20.5
21	9.4	F	18	59	4.6	g B P	34.8
	3.2	F	18	65	3.5	cor	15
22	9.1	F	17	64	4.7	cor	37.2
	3.7	F	18	69	4.6	cor	34.8
23	9.0	C′	18	60	5.2	w P cor	48.2
	6.5	F	18	59	4.6	w r g	34.8
24	9.3	F	17	59	6.1	w r g	73.3
	6.7	F	17	60	4.1	cor	24
25	9.3	F	17	65	6.2	w r g	76.5

TABLE 48.—Continued.

Date.	Time.	Weather.	°C.	°F.	s.	Corona.	$n \times 10^{-3}$.
1905.	*Hours.*						
May 25	3.3	F	18	69	4.8	w B P	39.5
26	9.2	F	18	72	4.8	w o g	39.5
	6.0	F	19	69	4.3	cor	28
27	8.8	C	19	69	3.8	cor	19
	6.7	R′	20	67	3.6	cor	16.2
28	9.8	F	20	77	4.3	w r g	28
	5.0	F	20	75	4.7	w r g	37.2
29	9.4	F	20	74	3.9	w r g	20.5
30	9.4	C	21	63	3.4	cor	13.8
	3.3	F	21	70	3.4	cor	13.8
31	9.0	F	20	64	3.2	cor	11.3
June 1	9.2	C	18	60	3.5	cor	15
	4.0	F	19	64	3.5	cor	15
2	9.9	F	19	65	4.7	cor	37.2
3	6.0	F	19	69	4.3	cor	28
4	9.5	F	19	70	4.8	w P cor	39.5
	5.0	F	19	71	3.7	cor	17.5
5	9.3	F	20	73	3.7	cor	17.5
6	9.9	R	21	63	2.9	cor	8.3
7	9.7	C	18	58	4.6	cor	34.8
8	9.2	R′	18	50	4.1	cor	24
	6.4	F	18	55	4.1	cor	24
9	9.4	F	17	66	5.4	w B cor	54.2
	5.8	F	19	69	4.0	cor	22
10	9.2	F	19	73	5.2	w	48.2
	6.1	F	20	75	4.0	cor	22
11	11.3	F	19	71	3.9	cor	20.5
	6.0	C	19	66	3.4	cor	13.8
12	9.5	R	19	65	4.7	cor	37.2
	5.5	R	19	62	3.9	cor	20.5
13	9.5	C	20	69	4.4	w r g	30
14	9.6	F	20	73	4.4	w r g	30
15	9.6	F	21	81	5.7	w r g	61.5
	6.0	F	22	76	3.8	cor	19
16	9.7	F	22	79	4.6	cor	34.8
	5.6	F	23	78	4.3	cor	28
17	9.5	F	22	73	4.2	cor	25.8
18	10.9	F	23	86	5.0	cor	43.8
	5.4	F	24	84	3.1	cor	10.2
19	10.8	F	20	62	2.8	cor	7.3
20	12.4	R	18	58	3.3	cor	12.5
22	10.4	C	20	69	4.1	cor	24
23	10.2	F	21	82	3.0	cor	9.3
24	10.0	C	21	74	4.8	w B P	39.5
	6.0	F	21	76	4.2	cor	25.8
25	11.4	F	21	82	3.7	cor	17.5
26	10.5	F	23	82	3.9	cor	20.5
27	10.0	F′	21	67	4.4	w r	30.0
28	11.0	F	20	70	4.8	g b P	39.5
	6.0	F	21	71	3.9	cor	20.5
29	10.3	F	21	76	4.8	w o cor	39.5
	6.6	F	21	77	3.6	cor	16.2
30	10.9	F	21	80	4.6	w y′	34.8
July 1	10.6	F	22	76	4.1	cor	24
	6.0	F	..	73	4.6	cor	34.8

TABLE 48.—Continued.

Date.	Time.	Weather.	°C.	°F.	*s*.	Corona.	$n \times 10^{-3}$.
1905.	*Hours.*						
July 2	12.0	R′	23	72	3.8	cor	19
3	11.3	C′	22	77	3.5	cor	15
4	11.2	F	23	86	4.7	w o	37.2
	6.5	F	23	81	3.1	cor	10.2
5	10.8	F	23	73	3.2	cor	11.3
6	9.8	C	23	72	2.9	cor	8.3
	5.5	F	23	72	3.9	cor	20.5
7	10.7	C′	23	79	5.9	w c g	68
8	12.0	C′	23	82	4.6	w r g	34.8
	4.0	F	..	80	4.2	w c g	25.8
9	11.0	F	24	85	4.6	g b p	34.8
	6.0	F	24	84	2.4	cor	4.6
11	10.3	F	26	85	4.7	w r g′	37.2
	4.5	C′	26	88	4.1	cor	24
12	10.6	F	26	89	5.4	w P cor	54.2
	6.0	F	27	85	3.7	cor	17.5
13	11.0	C′	26	88	4.9	w B cor	41.7
	5.7	F	..	84	3.7	cor	17.5
14	10.0	F	26	84	4.7	g B P	37.2
	5.5	F	27	83	4.4	w r	30
15	10.4	F	26	82	4.0	cor	22
	....	F	26	..	3.1	cor	10.2
16	10.7	F	25	78	3.8	w r	19
17	12.5	R′	26	85	3.5	cor	15
	5.3	R′	26	90	4.1	w r g	24
18	10.7	F	26	91	4.7	....	37.2
19	10.7	F	27	92	4.1	cor	24
	6.0	R	28	84	4.1	cor	24
20	10.5	F	27	86	4.2	cor	25.8
	6.0	F	27	82	3.3	cor	12.5
21	10.6	F	26	77	4.3	w o	28
	6.0	F	26	79	3.0	cor	9.3
22	10.5	F	25	80	5.5	w c g	56.2
	6.0	C	..	73	3.0	cor	9.3
23	10.3	R	25	65	2.2	cor	3.3
	6.5	C	..	67	1.8	cor	1.9
24	10.3	C	23	73	4.0	cor	22
25	10.2	C	23	77	4.5	w o cor	32.4
	6.0	F	23	77	3.7	cor	17.5
27	10.5	F	22	80	4.2	w r g	25.8
	4.7	F	23	81	4.6	w r g	34.8
29	9.8	C	23	76	2.6	cor	5.9
	4.6	R	24	73	3.5	w r g	15
30	10.6	R	..	75	2.2	cor	3.3
	6.0	R′	24	70	2.4	cor	4.6
31	10.3	C	23	66	2.7	cor	6.6
	4.3	C	23	67	2.8	cor	7.3
Aug. 1	10.4	R	22	63	3.2	cor	11.3
	6.0	R	21	65	3.2	cor	11.3
2	10.0	F	21	76	4.6	w r g	34.8
	6.0	C′	22	75	3.6	cor	16.2
3	9.6	F	21	75	5.6	w c g	58.7
	12.7	F	21	81	5.2	w P cor	48.2
	5.1	F	..	76	4.1	cor	24
4	9.7	F	21	78	4.5	g B P	32.4

TABLE 48.—Continued.

Date.	Time.	Weather.	°C.	°F.	*s*.	Corona.	$n \times 10^{-3}$.
1905.	*Hours.*						
Aug. 4	5.5	F	22	75	4.3	cor	28
5	9.7	C'	23	77	3.7	cor	17.5
	6.0	F	23	73	3.4	cor	13.8
6	10.7	F	23	80	4.0	cor	22
	6.0	F	23	76	3.2	cor	17.5
7	9.4	F	23	82	4.6	w r g	34.8
	....	R'	24	79	3.9	....	20.5
8	10.0	R'	24	77	4.3	w r g	28
	6.0	C'	25	80	3.9	....	20.5
9	9.6	C	24	76	3.6	....	16.2
	6.4	R	25	73	4.3	w r g	28
10	9.6	F	24	81	4.6	g B P	34.8
	6.0	C	..	79	4.6	w r g	34.8
11	9.8	C'	25	80	4.7	w o cor	37.2
	6.0	F	27	80	3.6	cor	16.2
12	10.5	C'	26	85	4.6	g B P	34.8
	6.0	C	26	79	3.3	cor	12.5
13	10.7	C	26	86	2.2	cor	3.3
	6.0	C'	26	78	3.2	cor	11.3
14	9.7	F	25	72	3.5	cor	15
15	10.7	R	23	66	3.5	cor	15
	6.3	R'	23	60	2.3	cor	4
16	11.6	R'	21	60	2.9	cor	8.3
17	10.5	F	20	70	6.5	w o g	86.5
	12.5	F	20	74	4.9	g' B P	41.7
	6.5	F	20	66	3.6	cor	16.2
18	10.4	F	20	70	4.4	w r g	30
19	9.8	F	20	68	2.7	cor	6.6
20	11.0	F	19	69	4.0	cor	22
21	10.5	F	20	77	4.0	cor	22
22	10.3	F	22	83	4.6	g B P	34.8
	6.2	C'	23	80	3.9	....	20.5
23	10.4	F	22	82	3.8	....	19
24	10.7	F	23	85	4.7	w o g	37.2
	6.0	R	25	79	4.6	g B P	34.8
25	10.4	R'	23	66	2.8	cor	7.3
	6.0	C	..	67	3.5	w r g	15
26	10.7	F	22	70	3.4	w r g	13.8
	6.0	F	22	68	2.5	cor	5.2
27	10.1	R'	21	60	2.4	cor	4.6
	6.5	C'	21	59	2.7	cor	6.6
28	9.8	F	19	65	4.5	g B P	32.4
	6.0	F	20	65	4.7	w r g	37.2
29	10.0	F	20	72	3.7	cor	17.5
	3.0	F	20	75	3.2	cor	11.3
30	10.8	C	20	73	3.9	cor	20.5
	3.7	R	21	74	4.4	w r g	30
31	10.0	R	20	64	3.1	cor	10.2
	3.0	C	20	69	2.5	cor	5.2
Sept. 1	10.6	C	20	69	4.4	w r g	30
	3.0	R	20	67	3.7	cor	17.5
2	9.7	C'	20	70	2.6	cor	5.9
	1.5	C'	20	70	3.5	w g r p	15
4	10.5	R	21	69	2.5	cor	5.2
	1.7	R'	21	72	2.0	cor	2.5

TABLE 48.—Continued.

Date.	Time.	Weather.	°C.	°F.	s.	Corona.	$n \times 10^{-3}$.
1905.	*Hours.*						
Sept. 7	10.3	F	20	71	3.6	cor	16.2
	3.3	C	20	71	3.7	cor	17.5
8	10.2	F	20	70	4.3	w r g	28
	2.5	F	20	74	3.1	cor	10.2
9	9.7	F	20	74	4.8	w r g	39.5
	2.5	F	20	78	4.0	w r g	22
11	9.9	F	21	72	4.2	cor	25.8
	2.5	C	21	71	3.8	cor	19
12	10.2	R	20	63	3.1	cor	10.2
	2.7	R	21	66	3.8	cor	19
13	10.3	C	20	70	3.3	cor	12.5
	2.4	C	20	74	3.8	cor	19
14	10.4	F	18	57	4.2	cor	25.8
	2.5	F	18	62	4.5	y g p	32.4
15	10.4	F	15	62	5.0	w r g	43.8
	2.5	F	17	64	3.8	cor	19.0
16	10.5	C	17	62	3.6	cor	16.2
	2.0	C	18	64	3.7	cor	17.5
18	10.0	C	18	68	3.6	cor	16.2
	3.6	C	19	71	3.8	cor	19
19	9.8	R	19	68	3.4	cor	13.8
	3.3	C	19	69	2.9	cor	8.3
20	10.3	C	19	67	3.5	cor	15
	3.7	C	20	69	3.8	cor	19
21	8.7	F	19	67	3.8	cor	19
	3.4	F	19	74	3.9	cor	20.5
22	9.8	F	19	70	4.7	y g p	37.2
	5.0	F	21	75	4.5	y g p	32.4
23	9.0	F	19	67	4.2	cor	25.8
25	11.0	F	18	61	4.4	cor	30
	2.7	F	18	62	3.9	cor	20.5
26	9.0	F	17	50	5.4	w r g	54.2
	3.7	F	17	58	4.7	cor	37.2
27	9.0	F	16	52	5.1	w r g	46
	5.5	F	16	60	5.6	w r g	58.7
28	9.5	F	16	65	4.6	y g p	34.8
	3.5	F	18	74	3.5	cor	15
29	9.2	F	17	63	5.5	w r g	56.2
	2.5	F	18	69	4.1	cor	24.0
30	9.0	F	18	63	4.4	y g p	30
	3.3	F	20	71	4.2	cor	25.8
Oct. 2	9.2	C	18	62	4.5	cor	32.4
	2.7	C	18	65	3.8	cor	19
3	10.0	F	19	72	3.4	cor	13.8
	2.8	F	19	75	3.8	cor	19
4	9.8	F	18	71	4.9	cor	41.7
	2.9	F	19	76	4.3	cor	28
5	10.5	F	19	76	4.9	y g p	41.7
6	9.3	F	18	58	4.7	y g p	37.2
	3.1	F	18	63	4.6	cor	34.8
7	9.1	F	17	56	5.2	cor	48.2
	2.6	F	17	63	4.8	cor	39.5
9	12.1	F	18	74	5.4	w r g	54.2
	4.5	F	18	71	4.7	cor	37.2
10	9.9	F	16	58	3.7	cor	17.5

Table 48.—Continued.

Date.	Time.	Weather.	°C.	°F.	*s*.	Corona.	$n \times 10^{-3}$.
1905.	*Hours.*						
Oct. 10	2.5	F	17	64	4.4	w r g	30
11	9.8	C	16	56	4.5	w r g	32.4
	2.2	C	16	58	4.7	w r g	37.2
12	9.0	F	16	54	4.3	w r g	28
	2.7	F	17	59	4.5	w r g	32.4
13	11.0	F	16	56	4.7	y g p	37.2
	2.6	C	16	58	4.8	y g p	39.5
14	10.0	F	17	61	4.8	y g p	39.5
	2.6	F	18	68	5.0	y g p	43.8
16	2.5	F	20	75	4.8	y g p	39.5
	4.7	F	20	73	5.2	w B cor	48.2
17	10.3	F	18	60	5.7	w r g	61.5
	2.7	F	18	63	5.0	w r g	43.8
18	9.2	F	18	61	4.5	cor	32.4
	2.7	F	18	66	4.6	cor	34.8
19	12.0	C	19	75	4.2	cor	25.8
	3.5	C	20	72	4.6	g P cor	34.8
20	11.6	R	19	60	3.7	cor	17.5
	2.6	R	18	60	3.7	cor	17.5
23	12.2	F	17	52	4.7	g B	37.2
	4.3	F	17	52	4.7	g B	37.2
24	10.2	F	16	54	4.7	cor	37.2
	2.7	F	17	61	4.7	y g p	37.2
25	12.1	F	17	55	4.7	w r g	37.2
	4.1	C	18	54	4.5	w B	32.4
26	2.7	C	18	46	4.6	w r g	34.8
	4.6	F	18	43	4.0	B g	22
27	11.0	F	17	50	5.4	g B P	54.2
	2.8	F	18	53	4.8	y g B	39.5
30	2.7	F	18	52	4.7	y g B	37.2
	4.3	F	18	47	4.6	w r g	34.8
31	11.5	C	18	54	4.8	w Br g	39.5
	3.7	C	19	54	4.5	w r g	32.4
Nov. 1	3.0	F	18	64	4.8	g B P	39.5
	5.6	F	19	54	4.7	w Br B	37.2
3	3.7	C	18	50	4.4	w r g	30
	5.0	C	18	48	4.6	w r g	34.8
4	10.2	F	18	53	4.7	w r g	37.2
	2.4	F	17	52	4.0	w Br B	22
6	2.7	R	17	51	4.3	w r g	28
7	10.5	F	18	48	5.7	w r g	61.5
	3.0	C	18	48	3.7	w Br B	17.5
8	3.0	C	19	48	4.7	w Br B	37.2
9	2.6	C	19	45	4.8	w Br B	39.5
10	11.1	F	21	46	5.3	g B P	50.5
	3.2	C	20	45	5.0	w Bz B	43.8
11	9.5	F	20	40	6.2	w r g	76.5
	10.5	F	20	42	6.8	y g	95
12	2.5	F	21	49	5.4	g B P	54.2
13	3.2	F	23	56	5.3	g B P	50.5
14	10.7	F	20	28	6.6	y g	90
16	2.5	C	20	51	4.9	w Br B	41.7
17	11.2	F	19	44	4.5	cor	32.4
	2.7	F	19	45	4.5	w e g	32.4
18	9.8	F	21	44	4.7	y g	37.2

TABLE 48.—Continued.

Date.	Time.	Weather.	°C.	°F.	*s*.	Corona.	$n \times 10^{-3}$.
1905.	*Hours.*						
Nov. 20	2.7	F	20	38	4.8	w Br B	39.5
21	10.6	F	20	46	6.5	y g	86.5
	3.3	F	21	52	6.0	w r g	70.5
22	12.1	F	20	52	6.1	w r g	73.3
	4.0	C	20	52	6.1	w r g	73.3
23	2.7	F	22	59	4.8	w Br B	39.5
24	2.5	F	22	63	4.8	w Br B	39.5
	5.3	F	22	55	4.7	w Br B	37.2
27	3.5	F	18	45	4.8	w Br B	39.5
	5.0	F	18	42	4.6	w Br B	34.8
28	10.4	C	19	38	4.7	w B g	37.2
	3.0	C	19	37	4.8	w B g	39.5
Dec. 4	12.1	F	21	39	4.2	cor	25.8
	2.7	F	20	37	4.3	w Br B	28
5	11.0	F	20	30	5.7	w r g	61.5
	2.7	F	19	36	5.4	w Br B	54.2
6	12.2	C	20	40	5.6	w r g	58.7
	3.0	C	20	40	4.6	w B g	34.8
7	2.7	F	19	46	4.8	w B g	39.5
8	11.2	F	22	50	4.9	w Br B	41.7
	3.2	F	22	53	5.4	w Br B	54.2
9	10.7	C	22	42	3.9	cor	20.5
11	3.0	C	20	34	5.6	w r g	58.7
12	10.7	C	21	28	4.7	w Br B	37.2
	2.7	F	20	35	5.0	w g B	43.8
13	12.2	F	22	44	6.1	w r g	73.3
	3.5	F	22	45	5.7	w g B	61.5
14	3.7	F	22	34	5.8	w g P	64.5
15	11.1	C	22	22	6.5	y g	86.5
16	3.5	C	21	32	5.0	w g P	43.8
18	4.0	F	23	46	6.7	g b P	92.5
19	10.5	F	23	42	4.7	w Br g	37.2
	2.5	C	23	46	4.7	w Br g	37.2
20	10.6	F	23	45	5.2	g b P	48.2
	3.9	F	23	47	4.8	w Br g	39.5
21	10.7	R	23	46	3.8	cor	19
	3.1	R′	23	52	4.9	w g P	41.7
1906.							
Jan. 1	3.7	F	23	36	4.6	w r g	32.4
2	10.7	F	22	31	5.7	w r g	61.5
	3.5	C	21	36	5.6	w B P	58.7
3	11.7	F	20	32	4.7	g B P	37.2
	3.4	C	20	34	4.8	w Br g	39.5
4	1.0	R′	22	58	5.0	g B P	43.8
	3.2	C	22	57	6.2	w r g	76.5
5	10.0	F	23	43	6.0	w r g	70.5
	2.7	F	22	44	5.3	w Br P	50.5
6	10.6	C	21	38	5.9	w r g	68
	4.3	F	20	37	5.9	w r g	68
8	12.5	C	19	27	4.7	w Br g	37.2
	4.5	Sn	20	26	4.7	w Br g	37.2
9	11.0	F	20	20	6.7	y g	92.5
	3.0	F	19	26	6.5	y g	86.5
10	4.0	F	18	25	6.4	w r g	83.5
11	12.2	F	19	32	5.9	w r g	68
	5.0	F	19	31	6.4	w r g	83.5
12	11.2	F	22	51	5.9	w r g	68

TABLE 48.—Continued.

Date.	Time.	Weather.	°C.	°F.	*s*.	Corona.	$n \times 10^{-3}$.
1906.	*Hours.*						
Jan. 12	4.8	F	22	47	5.6	w r g	58.7
13	10.5	F	21	38	4.5	cor	32.4
	3.3	C	21	36	3.8	w Br P	19
15	10.0	F	21	31	4.9	w Br P	41.7
16	11.5	R′	20	49	4.8	w r g	39.5
	3.5	R′	22	49	5.5	g B P	56.2
17	10.1	F	20	39	6.0	w r g	70.5
	3.5	F	18	40	4.7	w Br B	37.2
18	12.3	R′	18	44	4.9	g P r	41.7
	4.8	C	19	43	5.1	w Br P	46
19	10.0	F	19	39	4.6	w Br g	34.8
	2.7	F	20	41	5.8	w Br P	64.5
20	10.4	C	20	35	4.8	g Br	39.5
	3.2	R′	20	40	4.9	g Br	41.7
22	12.5	C	23	53	4.5	w Br g	32.4
	4.0	F	22	51	4.7	w Br g	37.2
23	10.3	F	22	63	5.0	w Br P	43.8
	5.0	F	23	63	5.1	w Br P	46
24	10.1	F	20	43	6.5	y g	86.5
25	9.8	F	20	26	5.3	w Br P	50.5
	3.2	F	19	26	4.5	w Br P	32.4
26	10.0	F	19	29	4.8	w Br g	39.5
	3.3	F	19	39	4.5	w Br g	32.4
27	10.2	F	20	37	6.3	y G	80.5
	4.4	F	20	46	4.9	w Br P	41.7
29	12.0	F	20	29	6.8	y G	95
	3.7	F	20	33	4.9	g Pr	41.7
30	10.5	F	20	41	6.1	w r g	73.3
	3.0	F	20	49	5.1	w Br B	46
31	12.3	F	21	52	4.7	w Br g	37.2
	3.3	F	21	49	4.5	w Br g	32.4
Feb. 1	12.2	F	21	43	6.0	G r g	70.5
	5.0	F	21	43	5.1	w Br P	46
2	11.0	F	19	20	6.5	y G	86.5
	5.0	F	17	14	5.5	w r b o g	56.2
3	10.2	F	18	9	6.2	w r g	76.5
	6.2	F	18	19	6.1	w r g	73.3
4	10.1	F	20	35	5.0	w P cor	43.8
	12.5	F	20	39	5.2	w P cor	48.2
	6.3	F	21	37	4.6	cor	34.8
5	5.0	..	22	39	4.7	cor	37.2
6	9.5	F	21	20	6.8	g B P	95
	11.3	F	21	21	6.4	w r g	83.5
	3.5	F	21	23	5.2	cor	48.2
7	10.5	Sn′	19	15	6.0	w r g	70.5
	12.1	Sn′	18	18	6.7	w o b g	92.5
	3.6	F	19	24	6.0	w r g	70.5
	6.1	..	19	22	5.9	w r g	68
8	9.5	F	20	19	5.9	w r g	68
	11.7	F	20	29	4.8	g B′	39.5
	3.0	F	19	34	4.8	w r g	39.5
	5.6	F	19	31	5.8	w r g	64.5
9	11.2	R	21	38	4.6	w r g	34.8
	4.8	C	21	35	4.8	w P cor	39.5
10	9.7	F	22	32	4.8	g B P	39.5
	12.8	F	21	36	4.8	g B P	39.5
	5.2	F	22	35	4.8	g B P	39.5

TABLE 48.—Continued.

Date.	Time.	Weather.	°C.	°F.	*s*.	Corona.	$n \times 10^{-3}$.
1906.	*Hours.*						
Feb. 11	9.8	F	22	22	6.5	yo bg	86.5
	12.0	F	..	27	6.0	w r g	70.5
	5.0	F	22	28	4.8	w r o g	39.5
12	9.6	F	22	34	5.3	w r g	50.5
	1.5	F	21	41	4.8	cor	39.5
	3.5	C	20	40	4.4	cor	30
13	12.2	R	22	42	4.6	g B P	34.8
	6.0	C	23	40	4.6	cor	34.8
14	12.3	C′	23	47	3.9	cor	20.5
	4.1	C	23	48	4.2	cor	25.8
15	1.0	C	20	24	6.8	g B P	95
	5.1	F	21	25	5.1	g Br	46
16	12.3	F	20	26	6.5	y g	86.5
	5.0	F	21	34	5.4	w r o b g	54.2
17	12.3	F	21	30	4.7	w Br g	37.2
	4.0	F	21	40	4.8	g Br	39.5
19	12.3	F	22	44	5.0	y g	43.8
	5.0	C	22	43	5.6	w Br P	58.7
20	11.3	F	22	42	5.8	w Br P	64.5
	4.7	F	22	47	5.0	w Br P	43.8
21	5.1	R	23	54	4.7	g B P	37.2
22	11.0	F	24	51	5.8	w r g	64.5
23	5.0	F	22	45	4.7	w Br g	37.2
26	4.3	F	21	45	4.9	w Br g	41.7
27	11.5	F	20	35	6.2	y g	76.5
	5.0	F	19	33	4.9	g Br	41.7
28	12.2	F	18	21	6.7	y g	92.5
	5.0	F	18	22	5.9	w r g	68
March 1	12.5	F	17	27	6.7	y g	92.5
	5.0	F	18	32	5.7	w r g	61.5
2	11.5	F	19	36	6.4	y g	83.5
	5.7	F	20	40	5.6	w r g	58.7
3	10.7	R′	21	36	4.5	cor	32.4
5	12.5	F	22	44	4.8	w b P	39.5
	4.7	F	22	45	4.8	w g p r	39.5
6	11.7	F	21	36	5.0	w b p	43.8
	5.0	F	21	38	5.9	w r g	68
7	12.5	C	20	43	5.1	w h p	46
	4.0	C	20	43	5.7	w r g	61.5
8	12.2	C	21	47	4.8	g br	39.5
	5.0	F	22	45	4.8	g br	39.5
10	11.5	F	19	44	6.0	y g	70.5
	3.5	F	20	47	4.8	w br P	39.5
12	1.2	F	18	40	5.7	w br g	61.5
	4.2	F	20	39	4.8	g br	39.5
13	5.0	C	19	32	5.0	w br g	43.8
14	4.0	F	20	33	5.0	g br	43.8
15	1.5	Sn	00	26	4.7	w br g	37.2
16	3.2	F	00	40	5.5	w br g	56.2
17	3.7	F	22	33	5.6	w br g	58.7
19	10.7	C	22	35	5.3	w br g	50.5
20	3.7	C	21	36	5.2	w br p	48.2
22	3.4	F	22	38	6.5	y g	86.5
23	10.8	F	22	24	6.2	y g	76.5
24	3.5	F	21	33	4.8	g br	39.5
26	10.8	C	22	36	4.9	w br p	41.7

TABLE 49.—Mean daily nucleations, corresponding to table 48.

Date.	$n \times 10^{-3}$	Date.	$n \times 10^{-3}$	Date.	$n \times 10^{-3}$
1905.		1905.		1905.	
May 4	11	June 28	30	Aug. 25	11
5	38	29	28	26	9
6	66	30	35	27	6
7	33	July 1	31	28	35
8	96	2	19	29	14
9	38	3	15	30	25
10	44	4	24	31	8
11	46	5	11	Sept. 1	24
12	32	6	14	2	10
13	21	7	68	4	4
14	14	8	30	7	17
15	22	9	20	8	19
16	13	11	31	9	31
17	18	12	36	11	22
18	26	13	30	12	15
19	34	14	34	13	16
20	46	15	16	14	29
21	25	16	19	15	31
22	36	17	19	16	17
23	42	18	37	18	18
24	49	19	24	19	11
25	58	20	19	20	17
26	34	21	19	21	20
27	18	22	33	22	35
28	33	23	3	23	26
29	21	24	22	25	25
30	14	25	25	26	46
31	11	27	30	27	52
June 1	15	29	10	28	25
2	37	30	4	29	40
3	28	31	7	30	28
4	29	Aug. 1	11	Oct. 2	26
5	18	2	25	3	16
6	8	3	65	4	35
7	35	4	30	5	42
8	24	5	16	6	36
9	38	6	20	7	44
10	35	7	28	9	46
11	17	8	24	10	24
12	29	9	22	11	35
13	30	10	35	12	36
14	30	11	26	13	38
15	40	12	24	14	42
16	31	13	7	16	44
17	26	14	15	17	53
18	27	15	9	18	34
19	7	16	8	19	30
20	12	17	72	20	17
21	. .	18	30	23	37
22	24	19	7	24	37
23	9	20	22	25	35
24	33	21	22	26	28
25	17	22	28	27	47
26	20	23	19	30	36
27	30	24	36	31	36

TABLE 49.—Continued.

Date.	$n \times 10^{-3}$	Date.	$n \times 10^{-3}$	Date.	$n \times 10^{-3}$
1905.		1905.		1906.	
Nov. 1	38	Dec. 21	30	Feb. 9	38
2	39	1906.		10	39
3	32	Jan. 1	32	11	65
4	30	2	60	12	40
6	28	3	38	13	35
7	39	4	60	14	23
8	37	5	60	15	70
9	39	6	68	16	70
10	47	8	37	17	38
11	70	9	89	19	51
13	50	10	83	20	54
14	90	11	76	21	37
16	42	12	63	22	64
17	32	13	26	23	37
18	37	15	42	26	42
20	39	16	48	27	59
21	78	17	54	28	75
22	73	18	44	Mar. 1	72
23	39	19	50	2	71
24	38	20	41	3	32
27	37	22	35	5	39
28	38	23	45	6	56
Dec. 4	27	24	86	7	54
5	58	25	41	8	39
6	47	26	36	10	55
7	39	27	61	12	50
8	48	29	68	13	44
9	20	30	60	14	44
11	59	31	35	15	37
12	40	Feb. 1	58	16	56
13	67	2	71	17	59
14	64	3	75	19	50
15	86	4	42	20	48
16	44	5	37	22	86
18	92	6	76	23	76
19	37	7	75	24	39
20	44	8	53	26	42

TABLE 50.—Mean monthly nucleations corresponding to table 48.

Date.	$n \times 10^{-3}$.	Date.	$n \times 10^{-3}$.
1905.		1905.	
November	53	August	23
December	69	September	24
January	66	October	35
February	71	November	45
March	47	December	50
April	40	1906.	
May	35	January	53
June	26	February	53
July	27	March	52

90. Mean monthly nucleations.—The data of table 48 suffice for the determination of the average nucleations per month, care being taken to omit the days on which no observations were taken. Table 50 contains the results.

These data are shown in the lower graphs of fig. 62. What is remarkable is the gradual rise of the curve to a persistent maximum reaching nearly into April. True, the winter was relatively mild and the spring relatively cold; but one would not be prepared to predict nucleations so uniformly maintained between November and April. The distribution is in fact peculiar, as may be seen by comparing it with the nucleation of the preceding years since 1902, in fig. 63. The uniformity of the new curve, the absence of maxima in December, are striking. One may note the upward march of the successive curves 1902–03, 1903–04, 1904–05.

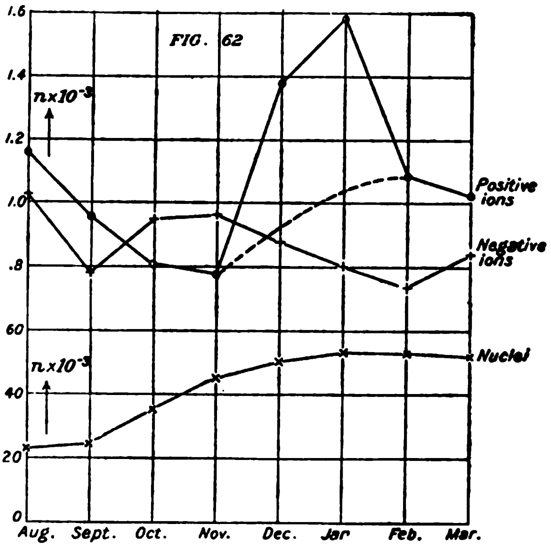

FIG. 62.—Average monthly ionization (thousands per cubic centimeter), positive and negative as stated, and nucleations (thousands per cubic centimeter), observed between August, 1905, and March, 1906.

91. Measurement of ionization.—To determine the number of ions in the atmosphere, Ebert's* well-known apparatus was used. This consists of a tubular condenser, the inner coat of which is charged and in contact with a graduated electroscope. The air to be examined is passed through the condenser by an aspirator-fan propelled by clockwork. The air delivery of the machine is also carefully standardized.

In order to test the same air which yielded the nuclei for the preceding measurement, the electrical apparatus (*E*, fig. 57*b*) was swung from the outside of a window on a long swivel bracket (*B*). In this way it could be drawn near the window for charging and examination with appropriate lenses or moved to a reasonable distance away from the window during the passage of the air to be tested. In winter all measurements must be made with a galvanoscope on the outside of the house. Thermometers are shown at *T*.

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* H. Ebert: Illus. Aëronaut. Mittheilungen, October, 1902, pp. 1–10.

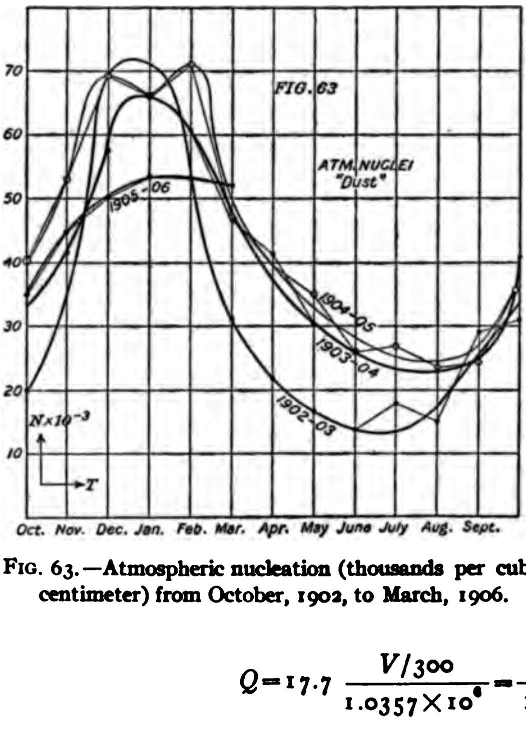

FIG. 63.—Atmospheric nucleation (thousands per cubic centimeter) from October, 1902, to March, 1906.

The difficulties encountered in using this apparatus in cold weather will be investigated later (section 94). Here some reference to its constants is in place. The quantity of air passed through the condenser in the fiducial time (about 10 minutes) was 1.0357 × 10^6 cubic centimeters; the capacity of the condenser 17.74 cm. Hence if *V* is the drop of potential in volts during the fiducial time specified,

$$Q = 17.7\,\frac{V/300}{1.0357\times 10^6} = \frac{V}{17.52\times 10^6}$$

denotes the charge in 1 cubic centimeter of air. As 3.4 × 10^{-10} is the electrostatic charge per electron,

$$n\times 10^{-3} = \frac{Q}{3.4\times 10^{-7}} = \frac{V}{6}, \text{ nearly,}$$

shows the number of ions per cubic centimeter. Measurements to find their velocity were not made, as this would have carried me too far from the purposes of this paper.

I may add that a similar apparatus was installed, in which the winter indraft of cold air (through a condenser), measured by an anemometer, was utilized. The object here was to determine the hourly variations of ionization. Though many observations were taken, their meaning is vitiated by the temperature discrepancy mentioned in section 94. For this reason, perhaps, a periodicity similar to the one discovered by Wood and Campbell (Nature, April, 1906, p. 583) with stagnant air was not detected.

92. Data for ionization.—In table 51 the date and hour are given in the first and second columns. The fall of potential, $V-v$ (v being the fall in the absence of the aspirator air current), in volts, during the ten minutes of observation, is shown in the fourth column, marked "volts." From this the charge (Q) in electrostatic units per cubic meter, and the number of ions (n) in thousands per cubic centimeter, are computed. The sign of the charges is indicated in each case, and q denotes their ratio (Q_+/Q_-). The correction (v) is regarded as negligible.

TABLE 51.

Date.	Time.	Volts.	Q.	$n \times 10^{-3}$.	Date.	Time.	Volts.	Q.	$n \times 10^{-3}$.
1905. July 26	4.0	3.7	+0.21	0.62	1905. Aug. 9	9.2	10.9	+0.62	1.82
		4.6	+ .26	.76			1.7	- .10	.29
		5.1	+ .29	.85			8.2	+ .47	1.38
		7.8	+ .45	1.32			5.2	- .30	.88
		6.1	+ .35	1.03			6.3	+ .36	1.05
	5	5.9	+ .34	1.00			4.2	- .24	.70
29	9.2	5.0	+ .29	.85			6.3	+ .36	1.05
		5.9	- .34	1.00			4.2	- .24	.70
	4.0	6.3	+ .36	1.02		12.3	5.2	+ .30	.88
		4.2	- .24	.70			6.3	- .36	1.05
31	10.0	7.7	+ .44	1.29	10	9.5	8.2	+ .47	1.38
		3.0	- .18	.52			5.2	- .30	.88
	3.0	7.8	+ .45	1.32		12	7.2	+ .41	1.20
		5.9	- .34	1.00			7.2	- .41	1.20
Aug. 1	10.0	2.6	+ .15	.44	11	10	6.3	+ .36	1.05
		2.6	- .15	.44			5.2	- .30	.88
	3.0	6.3	+ .36	1.02		12.3	8.2	+ .47	1.38
		8.1	- .46	1.35			5.2	- .30	.88
2	9.2	6.9	+ .39	1.14	12	9.0	6.3	+ .36	1.05
		5.6	- .32	.94			6.3	- .36	1.05
	4.0	5.9	+ .34	1.00		12.0	5.2	+ .30	.88
		3.1	- .18	.52			6.3	- .36	1.05
3	10.0	8.2	+ .47	1.38	14	9.4	11.9	+ .68	2.00
		5.5	- .31	.91			11.0	- .63	1.85
	4.3	6.7	+ .38	1.11		11.3	13.8	+ .79	2.32
		4.4	- .25	.73			11.0	- .63	1.85
4	10.0	5.3	+ .30	.88		12.3	11.0	+ .63	1.85
		4.4	- .25	.73			11.0	- .63	1.85
	4.3	2.6	+ .15	.44	15	10	10	+ .57	1.67
		4.8	- .27	.79			8.2	- .47	1.38
5	10.0	4.2	+ .24	.70			10.0	+ .57	1.67
		5.3	- .30	.88			8.2	- .47	1.38
	4.0	4.6	+ .26	.76			9.1	+ .52	1.52
		6.5	- .37	1.08			27.8	....	....
7	9.4	10.0	+ .57	1.67		12.3	9.1	+ .52	1.52
		6.7	- .38	1.11			9.1	- .52	1.52
	12.3	9.0	+ .51	1.50	16	10	8.2	+ .47	1.38
		9.5	- .54	1.58			5.2	- .30	.88
8	10.0	5.5	+ .31	.91		1.0	10.0	+ .57	1.67
		3.2	- .18	.52			7.2	- .41	1.20
9	9.2	6.3	+ .36	1.05	17	10.0	8.2	+ .47	1.38
		5.5	- .31	.91			5.2	- .30	.88

TABLE 51.—Continued.

Date.	Time.	Volts.	*Q*.	$n \times 10^{-3}$.	Date.	Time.	Volts.	*Q*.	$n \times 10^{-3}$.
1905.					1905.				
Aug. 17	12.3	10.0	+0.57	1.67	Sept. 2	9.7	3.7	−0.21	0.61
		10.0	− .57	1.67		1.4	6.0	+ .34	1.00
18	10.0	8.2	+ .47	1.38			2.2	− .12	.37
		9.1	− .52	1.52	4	10.5	5.1	+ .29	.85
	12.0	9.1	+ .52	1.52			2.8	− .16	.47
		9.1	− .52	1.52		1.7	5.4	+ .31	.91
19	9.0	10.0	+ .57	1.67			10.4	− .59	1.74
		9.1	− .52	1.52	7	10.3	4.8	+ .27	.80
	12.0	....	....	....			5.3	− .30	.88
		....	....	....		3.3	5.4	+ .31	.91
21	10.0	8.2	+ .47	1.38			4.2	− .24	.70
		9.1	− .52	1.52	8	10.2	7.1	+ .40	1.18
	1.0	7.2	+ .41	1.20			6.5	− .37	1.09
		2.1	− .12	.35		2.5	8.6	+ .49	1.44
22	10	6.3	+ .36	1.05			9.5	− .54	1.59
		6.3	− .36	1.05	9	9.7	5.0	+ .28	.84
	1.0	3.1	+ .18	.52			6.4	− .36	1.06
		4.2	− .24	.70		2.2	8.9	+ .51	1.50
23	9.3	10.0	+ .57	1.67			4.2	− .24	.70
		8.2	− .47	1.38	11	9.9	3.7	+ .21	.61
	12.0	7.2	+ .41	1.20			4.1	− .23	.69
		10.0	− .57	1.67		2.4	2.3	+ .13	.38
24	10.0	6.3	+ .36	1.05			2.8	− .16	.47
		6.3	− .36	1.05	12	10.1	10.8	+ .61	1.79
	12.0	4.2	+ .24	.70			1.9	− .11	.32
		5.2	− .30	.88		2.7	2.2	+ .12	.36
25	10.0	5.2	+ .30	.88			3.3	− .19	.56
		3.1	− .18	.52	13	10.3	4.8	+ .27	.79
	1.0	8.2	+ .47	1.38			4.0	− .23	.68
		6.3	− .36	1.05		2.3	4.2	+ .24	.70
26	9.0	8.2	+ .47	1.38			3.0	− .17	.50
		6.3	− .36	1.05	14	10.4	9.2	+ .52	1.53
	12.0	9.1	+ .52	1.52			6.7	− .38	1.12
		8.2	− .47	1.38		2.5	8.2	+ .47	1.38
28	10.4	6.2	− .35	1.05			7.6	− .43	1.25
		3.4	+ .19	.56	15	10.4	6.0	+ .34	1.00
	2.7	2.4	− .14	.41			7.7	− .44	1.29
		3.2	+ .18	.54		2.5	10.1	+ .57	1.68
29	9.9	3.7	+ .21	.63			3.5	− .20	.59
		3.7	− .21	.63	16	10.5	4.2	+ .24	.70
	2.6	5.0	+ .29	.86			2.4	− .14	.41
		4.5	− .25	.76		2.0	8.3	+ .47	1.40
30	10.5	4.8	+ .27	.79			2.4	− .14	.41
		3.0	− .17	.48	18	10.0	2.8	+ .16	.47
	2.6	4.5	+ .25	.76			5.3	− .30	.88
		5.1	− .29	.85		3.5	8.3	+ .47	1.40
31	10.0	3.0	+ .17	.50			2.8	− .16	.47
		5.6	− .32	.94	19	9.8	7.7	+ .44	1.29
	2.7	5.9	+ .34	1.00			1.8	− .10	.31
		4.2	− .24	.71		3.3	3.3	+ .19	.56
Sept. 1	10.5	5.4	+ .31	.91			2.3	− .13	.38
		4.7	− .27	.79	20	10.2	3.5	+ .20	.59
	3	6.8	+ .39	1.14			1.2	− .07	.20
		.4	− .23	.67		3.7	4.7	+ .27	.79
2	9.7	5.1	+ .29	.85			4.2	− .24	.70

TABLE 51.—Continued.

Date.	Time.	Volts.	Q.	$n \times 10^{-3}$.	Date.	Time.	Volts.	Q.	$n \times 10^{-3}$.
1905. Sept. 21	8.7	8.3	+0.47	1.40	1905. Oct. 7	2.6	3.5	−0.20	0.59
		4.2	− .24	.70	9	12 1	8.7	+ .50	1.46
	3.5	4.5	+ .26	.76			7.2	− .41	1.20
		4.6	− .26	.76		4.5	16.6	+ .95	2.79
22	9.8	1.9	+ .11	.32			2.4	− .14	.41
		2.6	− .15	.44	10	9.9	2.8	+ .16	.47
	5.0	2.8	+ .16	.47			4.8	− .27	.79
		2.4	− .14	.41		2.5	4.2	+ .24	.70
23	9.0	7.8	+ .44	1.30			8.1	− .46	1.35
		7.7	− .44	1.29	11	9.8	6.0	+ .34	1.00
25	11.0	8.3	+ .47	1.40			8.9	− .51	1.50
		9.5	− .54	1.59		2.2	2.3	+ .13	.38
	2.7	5.3	+ .30	.88			4.2	− .24	.70
		10.1	− .58	1.71	12	9.0	3.4	+ .19	.57
26	9.0	4.5	+ .26	.76			8.9	− .51	1.50
		4.1	− .23	.69		2.7	6.3	+ .36	1.02
	3.7	6.8	+ .39	1.14			7.7	− .44	1.29
		9.3	− .53	1.56	13	11.0	3.7	+ .21	.61
27	9.0	4.5	+ .26	.76			8.9	− .51	1.50
		2.7	− .15	.46		2.6	1.4	+ .08	.23
	5.5	1.1	+ .06	.19			3.0	− .17	.48
		3.5	− .20	.59	14	10.0	7.2	+ .41	1.20
28	9.5	3.7	+ .21	.61			7.1	− .40	1.18
		4.8	− .27	.79		2.6	4.9	+ .28	.82
	3.4	8.3	+ .47	1.40			4.2	− .24	.70
		5.4	− .31	.91	16	2.5	5.9	+ .34	1.00
29	9.2	7.0	+ .40	1.17			3.7	− .21	.61
		6.8	− .39	1.14		4.7	1.4	+ .08	.23
	2.5	2.4	+ .14	.41			2.4	− .14	.41
		1.8	− .10	.31	17	10.3	6.1	+ .35	1.03
30	9.0	1.9	+ .11	.32			7.4	− .42	1.23
		3.0	− .17	.48		2.7	7.5	+ .43	1.26
	3.2	3.7	+ .21	.61			3.5	− .20	.59
		1.4	− .08	.23	18	9.2	3.0	+ .17	.48
Oct. 2	9.1	2.3	+ .13	.38			8.0	− .46	1.35
		2.4	− .14	.41		2.7	2.4	+ .14	.41
	2.7	1.8	+ .10	.31			2.4	− .14	.41
		2.4	− .14	.41	19	12	4.2	+ .24	.70
3	10.0	3.6	+ .20	.60			7.4	− .42	1.23
		3.0	− .17	.50		3.5	6.7	+ .38	1.12
	2.8	7.9	+ .45	1.31			4.8	− .27	.79
		4.8	− .27	.79	20	11.6	6.4	+ .36	1.07
4	9.8	3.6	+ .20	.60			2.8	− .16	.47
		4.2	− .24	.70		2.6	6.5	+ .37	1.09
	2.9	3.0	+ .17	.48			1.9	− .11	.32
		3.6	− .20	.60	23	12.2	4.2	+ .24	.70
5	10.5	2.4	+ .14	.41			6.9	− .39	1.14
		6.0	− .34	1.00		4.3	6.4	+ .36	1.07
6	9.2	6.6	+ .38	1.11			7.7	− .44	1.29
		9.5	− .54	1.59	24	10.2	1.7	+ .10	.29
	3.1	7.2	+ .41	1.20			3.3	− .19	.56
		10.4	− .59	1.74		2.7	3.1	+ .18	.52
7	9.2	6.5	+ .37	1.09			1.8	− .10	.31
		6.6	− .38	1.11	25	12.1	6.2	+ .35	1.05
	2.6	3.6	+ .20	.60			8.2	− .47	1.38

TABLE 51.—Continued.

Date.	Time.	Volts.	Q.	$n \times 10^{-3}$.	Date.	Time.	Volts.	Q.	$n \times 10^{-3}$.
1905.					1905.				
Oct. 25	4.0	1.4	+0.08	0.23	Nov. 14	10.7	5.4	−0.31	.91
		3.6	− .20	.60	16	2.5	3.3	+ .19	.56
26	2.7	5.6	+ .32	.94			6.8	− .39	1.14
		11.3	− .65	1.91	17	11.2	3.6	+ .20	.60
	4.6	6.9	+ .39	1.14			4.2	− .24	.70
		9.6	− .55	1.62		2.7	2.8	+ .16	.47
27	11.0	5.6	+ .32	.94			8.4	− .48	1.41
		8.3	− .47	1.40	18	9.8	4.6	+ .26	.76
	2.8	6.0	+ .34	1.00			10.4	− .59	1.74
		4.2	− .24	.71	20	2.7	1.7	+ .10	.29
30	2.5	3.4	+ .19	.57			8.1	− .46	1.35
		10.5	− .60	1.76	21	10.6	2.4	+ .14	.41
	4.7	6.3	+ .36	1.02			7.1	− .40	1.18
		3.0	− .17	.48		3.2	5.3	+ .30	.88
31	11.4	2.4	+ .14	.41			5.4	− .31	.91
		8.9	− .51	1.50	22	12.1	7.7	+ .44	1.29
	3.7	3.0	+ .17	.48			6.6	− .38	1.11
		7.7	− .44	1.29		4.0	1.8	+ .10	.31
Nov. 1	3.0	8.7	+ .50	1.46			6.8	− .39	1.14
		2.8	− .16	.47	23	2.7	5.9	+ .34	1.00
	5.6	6.7	+ .38	1.12			1.8	− .10	.31
		6.0	− .34	1.00	24	2.5	3.7	+ .21	.61
2	2.4	6.7	+ .38	1.12			3.0	− .17	.48
		9.5	− .54	1.59		5.3	1.8	+ .10	.31
3	2.7	1.8	+ .10	.31			2.3	− .13	.38
		3.0	− .17	.50	27	3.4	5.3	+ .30	.88
	5.0	6.0	+ .34	1.00			6.6	− .38	1.11
		2.4	− .14	.41		5.3	7.8	+ .45	1.32
4	10.2	1.4	+ .08	.23			2.3	− .13	.38
		2.4	− .14	.41	28	10.5	1.8	+ .10	.31
	2.4	2.8	+ .16	.47			4.5	− .26	.76
		2.2	− .12	.36		3.0	4.8	+ .27	.79
6	3.0	7.2	+ .41	1.20			5.7	− .32	.96
		3.0	− .17	.50	Dec. 4	12.0	5.4	+ .31	.91
7	10.6	6.2	+ .35	1.05			4.2	− .24	.70
		9.5	− .54	1.59		2.7	2.4	+ .14	.41
	2.8	5.8	+ .33	.97			11.9	− .68	2.0
		4.4	− .25	.73	5	11.0	12.7	+ .73	2.15
8	3.0	5.3	+ .30	.88			11.9	− .68	2.00
		3.0	− .17	.50		2.7	12.0	+ .68	2.01
9	2.5	2.3	+ .13	.38			6.9	− .39	1.14
		11.1	− .63	1.85	6	12.2	9.5	+ .54	1.59
10	11.1	4.7	+ .27	.79			3.0	− .17	.50
		8.3	− .47	1.40		2.7	2.8	+ .16	.47
	3.0	1.8	+ .10	.31			3.6	− .20	.60
		3.6	− .20	.60	7	2.7	10.5	+ .60	1.76
11	10.5	3.9	+ .22	.65			4.5	− .26	.76
		5.4	− .31	.91	8	11.2	9.5	+ .54	1.59
	2.5	4.8	+ .27	.79			2.4	− .14	.41
		8.1	− .46	1.35		3.2	7.3	+ .42	1.24
13	12.4	6.8	+ .39	1.14			2.3	− .13	.38
		6.0	− .34	1.00	9	10.7	6.7	+ .38	1.12
	3.2	.9	+ .05	.16			5.9	− .34	1.00
		5.6	− .32	.94	11	3.0	7.6	+ .43	1.25
14	10.7	9.8	+ .56	1.65			4.9	− .28	.82

TABLE 51.—Continued.

Date.	Time.	Volts.	Q.	$n\times10^{-3}$.
1905. Dec. 12	10.7	11.0	+0.63	1.85
		1.4	− .08	.23
	2.7	4.7	+ .27	.79
		5.9	− .34	1.00
13	12.2	11.3	+ .65	1.91
		9.5	− .54	1.59
	3.5	7.7	+ .44	1.29
		4.4	− .25	.73
14	3.7	1.9	+ .11	.32
		4.7	− .27	.79
15	11.0	12.7	+ .73	2.15
		4.7	− .27	.79
16	3.5	14.3	+ .82	2.41
		3.4	− .19	.57
18	4.0	8.4	+ .48	1.41
		2.9	− .16	.49
19	10.5	6.7	+ .38	1.12
		4.1	− .23	.69
	2.4	7.6	+ .43	1.25
		14.8	− .84	2.47
20	10.5	6.8	+ .39	1.14
		4.9	− .28	.82
	3.9	6.0	+ .34	1.00
		4.7	− .27	.79
21	10.5	11.3	+ .65	1.91
		6.5	− .37	1.09
	3.0	3.7	+ .21	.61
		3.0	− .17	.48
1906. Jan. 1	3.7	11.3	+ .65	1.91
		4.6	− .26	.76
2	10.7	19.0	+2.09	6.01
		10.2	− .58	1.70
	3.5	18.0	+1.03	3.01
		4.4	− .25	.73
3	11.7	9.5	+ .54	1.59
		7.0	− .40	1.17
	3.3	9.7	+ .55	1.62
		1.4	− .08	.23
4	12.8	8.1	+ .46	1.35
		2.4	− .14	.41
	3.2	2.3	+ .13	.38
		4.2	− .24	.70
5	10.0	11.9	+ .68	2.00
		7.5	− .43	1.26
	2.7	10.1	+ .57	1.68
		13.7	− .78	2.29
6	10.6	9.2	+ .52	1.53
		5.4	− .31	.91
	4.3	11.3	+ .65	1.91
		5.8	− .33	.97
8	12.5	12.5	+ .71	2.01
		6.5	− .37	1.09
	4.5	13.0	+ .74	2.02
		7.2	− .41	1.20

Date.	Time.	Volts.	Q.	$n\times10^{-3}$.
1906. Jan. 9	11.0	9.3	+0.53	1.56
		3.8	− .22	.65
	3.0	10.5	+ .60	1.76
		5.1	− .29	.85
10	3.5	10.6	+ .60	1.78
		1.4	− .08	.23
11	12.5	9.7	+ .55	1.62
		4.2	− .24	.70
	4.7	13.4	+ .76	2.02
		2.4	− .14	.41
12	11.2	4.1	+ .23	.69
		3.2	− .18	.54
	4.8	6.5	+ .37	1.09
		3.4	− .19	.57
13	10.5	16.0	+ .91	2.68
		6.7	− .38	1.12
	3.2	?21.5	+1.23	3.62
		2.3	− .13	.38
15	10.0	6.7	+ .38	1.12
		5.9	− .34	1.00
16	11.5	6.6	+ .38	1.11
		1.9	− .11	.32
	3.4	5.7	+ .32	.96
		3.7	− .21	.63
17	10.0	7.0	+ .40	1.17
		1.9	− .11	.32
	3.5	7.0	+ .40	1.17
		5.3	− .30	.88
18	12.2	7.1	+ .40	1.18
		1.7	− .10	.29
	4.8	3.4	+ .19	.57
		1.1	− .06	.18
19	9.9	6.6	+ .38	1.11
		4.2	− .24	.70
	2.7	9.7	+ .55	1.62
		7.7	− .44	1.29
20	10.3	7.1	+ .40	1.18
		3.1	− .18	.52
	3.2	2.8	+ .16	.47
		3.7	− .21	.61
22	12.5	7.8	+ .45	1.32
		5.4	− .31	.91
	4.0	4.7	+ .27	.79
		6.3	− .36	1.02
23	10.3	5.3	+ .30	.88
		3.4	− .19	.57
	5.0	8.1	+ .46	1.35
		2.3	− .13	.38
24	10.0	8.4	+ .48	1.41
		9.6	− .55	1.62
25	9.8	11.2	+ .64	1.88
		4.3	− .24	.73
	3.1	7.2	+ .41	1.20
		4.2	− .24	.70
26	10.0	8.9	+ .51	1.50

TABLE 51.—Continued.

Date.	Time.	Volts.	Q.	$n \times 10^{-3}$.	Date.	Time.	Volts.	Q.	$n \times 10^{-3}$.
1906.					1906.				
Jan. 26	10.0	1.9	−0.11	0.32	Feb. 8	9.8	4.8	+0.27	0.79
	3.3	11.3	+ .65	1.91		12.6	5.2	+ .30	.88
		3.0	− .17	.48			11.2	− .64	1.88
27	10.2	7.5	+ .43	1.26		3.4	8.6	+ .49	1.45
		4.9	− .28	.82			3.3	− .19	.56
	4.4	8.0	+ .46	1.35		4.8	3.8	+ .22	.64
		1.8	− .10	.31			3.9	− .22	.66
29	12	16.1	+ .92	2.70	9	11.5	7.7	+ .44	1.30
		5.0	− .28	.84			6.2	− .35	1.04
	3.7	10.0	+ .57	1.67			1.9	+ .11	.33
		6.2	− .35	1.05		4.9	5.9	+ .34	1.00
30	10.5	5.3	+ .30	.88			1.4	− .08	.23
		7.2	− .41	1.20	10	9.9	5.4	+ .31	.91
	3.0	4.8	+ .27	.79			3.3	+ .19	.56
		4.2	− .24	.70		10.6	2.8	− .16	.47
31	12.3	8.3	+ .47	1.40		10.6	4.2	+ .24	.71
		7.5	− .43	1.26		12.5	8.1	+ .46	1.37
	3.2	8.9	+ .51	1.50			4.6	− .26	.76
		6.5	− .37	1.09		5.0	3.7	+ .21	.62
Feb. 1	12.0	11.1	+ .63	1.87			3.3	− .19	.56
		6.9	− .39	1.14	11	10.2	12.3	+ .70	2.06
	5.0	6.8	+ .39	1.14			6.0	− .34	1.00
		1.8	− .10	.31			6.5	+ .37	1.10
2	11.0	12.3	+ .70	2.07		11	6.4	− .37	1.08
		7.0	− .40	1.17			6.7	+ .38	1.12
	5.0	11.9	+ .68	2.00		4.5	7.0	+ .40	1.18
		2.4	− .14	.41			4.3	− .24	.73
3	10.2	9.5	+ .54	1.59			6.1	+ .34	1.03
		4.7	− .27	.79	12	9.7	8.7	+ .50	1.47
	6.0	1.8	+ .17	.52			7.8	− .45	1.30
		3.5	− .20	.59		12	7.7	+ .44	1.30
4	10.0	8.6	+ .49	1.44			8.7	− .50	1.47
		6.8	− .39	1.15		3	7.8	+ .45	1.32
	12.4	3.7	+ .21	.62			3.4	− .19	.57
		8.4	− .48	1.40	13	12.5	5.4	+ .31	.91
	6.2	5.6	+ .32	.94			.0	.0	.0
		6.0	− .34	1.00		5.7	4.7	+ .27	.79
5	5.0	9.0	+ .51	1.50			3.0	− .17	.50
		1.4	− .08	.23	14	12.5	5.4	+ .31	.91
6	9.5	7.7	+ .44	1.30			.5	− .03	.09
		2.9	− .17	.50		4.7	1.6	+ .09	.28
	11.6	7.6	+ .43	1.28			2.9	− .16	.48
		1.4	− .08	.23	15	12.5	4.2	+ .24	.70
	12.1	4.4	+ .25	.73			2.8	− .16	.47
		4.1	+ .23	.69		5.2	7.1	+ .40	1.18
	3.0	2.2	− .13	.38			3.4	− .19	.57
		.9	+ .05	.15	16	12.5	7.3	+ .42	1.24
7	9.9	2.5	+ .14	.43			7.1	− .40	1.18
		5.3	− .30	.89		5.0	5.0	+ .29	.86
	12.	10.3	+ .59	1.74			3.7	− .21	.61
		10.1	− .58	1.70	17	12.2	4.2	+ .24	.70
	3.6	9.0	+ .51	1.51			2.8	− .16	.47
		4.1	− .23	.69		3.4	4.2	+ .24	.71
	6.2	2.8	+ .16	.47			1.7	− .10	.29
		5.4	− .31	.89	19	12.2	5.3	+ .30	.89

TABLE 51.—Continued.

Date.	Time.	Volts.	Q.	$n \times 10^{-3}$.	Date.	Time.	Volts.	Q.	$n \times 10^{-3}$.
1906.					1906.				
Feb. 19	12.2	4.4	−0.25	0.73	Mar. 6	5.0	4.0	+0.22	0.66
	5.0	3.8	+ .22	.64			3.1	− .18	.52
		3.4	− .19	.57	7	12.5	7.9	+ .45	1.32
20	11.2	8.7	+ .50	1.47			6.2	− .35	1.05
		4.3	− .24	.73		3.7	4.0	+ .22	1.17
	5.0	4.7	+ .27	.79			2.8	− .16	.47
		2.8	− .16	.47	8	12.2	7.3	+ .42	2.15
21	5.3	5.4	+ .31	.91			4.2	− .24	.71
		4.2	− .24	.71		5.0	3.7	+ .21	1.09
22	12.0	6.8	+ .39	1.15			4.2	− .24	.71
		6.0	− .34	1.00	10	11.5	6.2	+ .35	1.05
23	4.7	6.0	+ .34	1.00			4.2	− .24	.71
		4.7	− .27	.79		3.5	5.1	+ .29	.85
26	4.3	8.1	+ .46	1.37			1.4	− .08	.23
		5.8	− .33	.97	12	1.2	8.7	+ .50	1.47
		6.7	+ .38	1.12			9.0	− .51	1.50
27	11.5	9.0	+ .51	1.50		4.2	5.2	+ .29	? .87
		5.5	− .31	.91			4.7	− .27	.79
	5.0	5.1	+ .29	.85	13	5	5.9	+ .34	1.00
		3.3	− .19	.56			3.6	− .20	.60
28	12.2	9.4	+ .54	1.59	14	4	4.8	+ .27	.79
		6.6	− .38	1.11			3.1	− .17	.50
	5.0	8.5	+ .48	1.43	15	1.5	7.0	+ .40	1.17
		5.6	− .31	.91			6.2	− .35	1.05
Mar. 1	12.5	9.4	+ .54	1.59	16	3.2	8.3	+ .47	1.38
		6.5	− .37	1.09			3.7	− .21	1.09
	5.0	5.9	+ .34	1.00	17	3.7	2.4	+ .14	.41
		6.0	− .34	1.00			2.6	− .15	.44
2	11.5	6.3	+ .36	1.06	19	10.7	6.2	+ .35	1.05
		5.7	− .32	.96			3.7	− .21	1.09
	5.7	3.3	+ .19	.56	20	3.7	3.4	+ .19	.57
		3.2	− .18	.54			4.4	− .25	.73
3	10.7	4.2	+ .24	.71	22	3.4	5.0	+ .28	.84
		9.3	− .53	1.57			5.2	− .30	.88
5	12.5	10.6	+ .61	1.79	23	10.7	7.9	+ .45	1.32
		7.5	− .43	1.26			6.7	− .38	1.12
	4.5	10.5	+ .60	1.76	24	3.5	2.8	+ .16	.47
		3.5	− .20	.59			2.8	− .16	.47
6	11.5	6.6	+ .38	1.11	26	10.8	6.4	+ .36	1.06
		4.8	− 27	.79			5.1	− .29	.85

93. Remarks on the tables.—Perhaps the most expeditious way of digesting this large body of observations is to plot them graphically (as above, figs. 58–61) in relation to time. This was carefully done throughout, and the statements now to be made refer to this summary. It is not probable that positive and negative ions will show the same fluctuations in number, but a general similarity in the trend of the curves may be anticipated.

Beginning with August, 1905, the positive and negative ionizations usually vary in the same sense, though rarely in the same absolute magnitude. There being but two observations, as a rule, for the day, the nature of the fluctuations is not referable to periods; and indeed there is as liable to be a rise as a fall of values during the middle hours of the day. Towards the end of the month and in the beginning of September there is an absence of agreement in the march of positive and negative ionizations. Frequently the variation of one ionization is apt to lag behind the other.

After the 7th of September the positive and negative variations tend to take the same sign again, but the agreement in the course of a month is less marked than before.

In October the earlier observations are as a rule in the same phase until October 10, where the first of a series of anomalies occurs, to be specially considered later (section 94). While the data throughout the remaining part of October are regular, there are similarly displaced variations towards the end, which run quite into the next month.

During November similarity of variation of the positive and negative ionization may still be recognized, but in December the divergence of data is so marked that it is not possible to coordinate them; and the same discrepancy shows itself in January, both as regards the signs of variations and their absolute values. One may note, moreover, that the positive curve (the observations for which were first taken) is more irregular in its march and fluctuates between relatively enormous values. Though there is some agreement in phase between January 18 and 25, the anomalies increase again at the close of the month.

The attempt was therefore made in February (section 94) to account for and remove these discrepancies, and though this was but partially successful, the positive and negative results during the remainder of the season again return to an unmistakable agreement in character. There is, moreover, a curious parallelism between the general march of the nucleation curves and the ionization after February 15 as far as March. In the latter month the positive and negative ionizations, though at first fluctuating and uncertain, are finally in very close agreement.

From what has been stated it appears that the positive results during December and January are liable to be untrustworthy. The negative results, which were taken after the positive, show less irregular fluctuation and are in a measure acceptable throughout the eight months of observation.

94. Errors of measurement.—The abnormal data during the occurrence of cold weather, and as a rule in December and January, show that some grave error must here have crept into the results. As every part of the condenser and appurtenances functioned faultlessly, this error is liable to be found in the galvanoscope. Changes of temperature produce vortical currents in the capsule which modify the deflections of the aluminum foils. In the mean ranges, one scale part of double deflection is equivalent to about 6 volts, or to 1,000 ions per cubic centimeter. Therefore, the presence of any secondary disturbance like the one in question is of very serious consequence. Prior to measurement, the apparatus was naturally left in the cold air out of doors until temperature uniformity was presumable; but this is not sufficient, as the special observations in the early part of February show, even for a galvanoscope dried with sodium.

Turning first to the leakages due to conduction, etc. (v in the above equation), direct experiments made at different times showed values of 0.073, 0.067, 0.120 volt per minute, or less than 0.9 volt for the ten minutes of observation. This is equivalent to an excess of 150 ions per cubic centimeter. As it is applied equally to the positive and to the negative ions, is independent of the size of the deflections, and the same no matter whether the deflections on both sides are equal or not, it has no bearing on the outstanding errors in question. It was not deducted from the ionizations (n) of table 53, which are therefore slightly too large.

Trials made between February 4 and 11 showed that in almost every case the first measurements (whether for positive or negative ions), even after the galvanoscope had been exposed to the cold air for some time, are too large. This discrepancy may at times extend to the second and third observations (February 6, 9, 11). Thus on February 9 the estimated positive ionization would be a thousand and zero, for instance. Usually, however, the second and third observations are liable to be trustworthy (February 6, 10, 11, etc.). Hence electroscopic apparatus which can not be left permanently out of doors, but is taken from a warm room into the cold atmosphere, even if it is sodium dried, is not liable to show warrantable results after mere waiting for uniform temperature. It seems additionally necessary to pass a large volume of cold air through the condenser, or to make successive measurements in series. The observer is usually in doubt, whenever the positive and negative ionizations differ widely, so that at least three tests must be made. The tendency of the apparatus to show spurious results is usually indicated by an inequality of deflections of the foils on either side of the vertical. They may increase to a maximum after charging and then decrease regularly. The latter probably finds an explanation in the gradual cessation of a down-pouring cold air current near the sides of the capsule of the galvanoscope, but the persistence of unequal deflections must follow from other causes. Remembering that the air is desiccated internally with metallic sodium, it seems hardly creditable that there can be a precipitation of moisture from this dried air on the aluminum foils; and yet the behavior is such as if a moisture gradient from the foil nearest the sodium to that more remote were permanently maintained. In such a case there would be slight but unequal precipitation of vapor on the two foils, in an apparatus passing from warm to cold, and persistence would be due to freezing. The only other explanation is the possibility of charges on the very cold glass and on other insulators which can not be earthed.

95. Mean daily ionization.—As in the preceding case, the observations were now averaged for single days. The results are given in detail in table 52. If given in the charts with the number of ions in thousands per cubic centimeter laid off vertically, very little that is new may be taken from these figures, and they are therefore omitted. They serve, however, as a basis for the monthly ionizations which follow, and in comparing the ionizations with the nucleation of the atmosphere these charts are useful. Thus, it would be difficult to detect synchronism in August, September, October, November, December; but from the middle of January to the end of February suspicions of this kind would be justified.

TABLE 52.—Mean daily ionizations corresponding to table 51.

Date.	Positive ions. $n \times 10^{-3}$	Negative ions. $n \times 10^{-3}$	Date.	Positive ions. $n \times 10^{-3}$	Negative ions. $n \times 10^{-3}$	Date.	Positive ions. $n \times 10^{-3}$	Negative ions. $n \times 10^{-3}$
1905.			1905.			1905.		
July 26	0.90	....	Aug. 28	0.55	0.73	Sept. 29	0.79	0.72
29	.93	0.85	29	.74	.69	30	.46	.36
31	1.30	.76	30	.78	.66	Oct. 2	.34	.41
Aug. 1	.73	.89	31	.75	.82	3	.95	.64
2	1.07	.73	Sept. 1	1.02	.73	4	.54	.65
3	1.24	.82	2	.62	.49	5	.41	1.00
4	.66	.76	4	.88	1.10	6	1.15	1.66
5	.73	.98	7	.85	.79	7	.84	.85
7	1.58	1.34	8	1.31	1.34	9	2.12	.80
8	.91	.52	9	1.17	.88	10	.58	1.07
9	1.20	.75	11	.49	.58	11	.69	1.10
10	1.29	1.04	12	1.07	.44	12	.79	1.39
11	1.21	.88	13	.75	.59	13	.42	.99
12	.96	1.05	14	1.45	1.18	14	1.01	.94
14	2.05	1.85	15	1.34	.94	16	.61	.51
15	1.59	1.42	16	1.05	.41	17	1.14	.86
16	1.52	1.04	18	1.43	.67	18	.44	.38
17	1.52	1.27	19	.92	.34	19	.91	1.01
18	1.45	1.52	20	.69	.45	20	1.08	.39
19	1.67	1.52	21	1.08	.73	23	.89	1.21
21	1.29	.93	22	.39	.42	24	.40	.43
22	.78	.87	23	1.30	1.29	25	.64	.99
23	1.43	1.52	25	1.14	1.65	26	1.04	1.76
24	.87	.96	26	.95	1.12	27	.97	1.08
25	1.13	.78	27	.47	.52	30	.79	1.12
26	1.45	1.21	28	1.00	.85	31	.44	1.39

TABLE 52.—Mean daily ionizations corresponding to table 51.—Continued.

Date.	Positive ions. $n \times 10^{-3}$	Negative ions. $n \times 10^{-3}$	Date.	Positive ions. $n \times 10^{-3}$	Negative ions. $n \times 10^{-3}$	Date.	Positive ions. $n \times 10^{-3}$	Negative ions. $n \times 10^{-3}$
1905.			1905.			1906.		
Nov. 1	1.29	0.73	Dec. 21	1.26	0.78	Feb. 9	0.87	0.63
2	1.12	1.59	1906.			10	.83	.59
3	.65	.45	Jan. 1	1.91	.76	11	1.29	.93
4	.35	.38	2	4.51	1.21	12	1.36	1.11
6	1.20	.50	3	1.60	.70	13	.85	.50
7	1.01	1.16	4	.86	.55	14	.59	.28
8	.88	.50	5	1.84	1.77	15	.94	.52
9	.38	1.85	6	1.72	.94	16	1.05	.89
10	.55	.50	8	2.01	1.14	17	.70	.38
11	.72	1.13	9	1.66	.75	19	.76	.65
13	.60	.97	10	1.78	.23	20	1.13	.60
14	1.65	.91	11	1.83	.55	21	.91	.71
16	.56	1.14	12	.89	.55	22	1.15	1.00
17	.53	1.05	13	3.15	.75	23	1.00	.79
18	.76	1.74	15	1.12	1.00	26	1.24	.97
20	.29	1.35	16	1.03	.47	27	1.17	.73
21	.64	1.04	17	1.17	.60	28	1.51	1.01
22	.80	1.13	18	.87	.23	Mar. 1	1.29	1.04
23	1.00	.31	19	1.36	.99	2	.81	.75
24	.46	.43	20	.82	.56	3	.71	1.57
27	1.10	.74	22	1.05	.96	5	1.78	.92
28	.55	.86	23	1.11	.47	6	.88	.65
Dec. 4	.66	1.35	24	1.41	1.62	7	1.24	.76
5	2.08	1.57	25	1.54	.71	8	1.62	.71
6	1.03	.55	26	1.70	.40	10	.95	.47
7	1.76	.76	27	1.30	.56	12	1.17	1.14
8	1.41	.39	29	2.18	.94	13	1.00	.60
9	1.12	1.00	30	.83	.95	14	.79	.50
11	1.25	.82	31	1.45	1.17	15	1.17	1.05
12	1.32	.61	Feb. 1	1.50	.72	16	1.38	1.09
13	1.60	1.16	2	2.03	.79	17	.41	.44
14	.32	.79	3	1.05	.69	19	1.05	1.09
15	2.15	.79	4	.93	1.18	20	.57	.73
16	2.41	.57	5	1.50	.23	22	.84	.88
18	1.41	.49	6	.83	.37	23	1.32	1.12
19	1.18	1.58	7	1.03	1.04	24	.47	.47
20	1.07	.81	8	.94	1.03	26	1.06	.85

96. Mean monthly ionizations and conclusion.—The straightforward way of arriving at a conclusion as to the presence or absence of a relation between the nucleation and the ionization of the atmosphere consists in comparing the average monthly values for both cases. This is done in table 53, and graphically in fig. 62.

The curve showing the distribution of negative ions is probably the more trustworthy, as these observations were made last. The positive distribution curve is too high in December and January for the reasons already stated, and its more probable course during these two months is indicated by the dotted line. It seems exceedingly curious that whereas the fluctuations of positive and negative ionization in successive observations, on the same or on succeeding days, usually show the same sign, although not the same absolute value, this is not in general the case with the monthly ionizations. The two curves of fig. 62 throughout the greater part of their course vary in opposite directions.

TABLE 53.—Mean monthly ionizations, corresponding to table 51.

Date.	Positive ions. $n \times 10^{-3}$	Negative ions. $n \times 10^{-3}$
1905.		
Aug.	1.16	1.02
Sept.	.95	.78
Oct.	.80	.94
Nov.	.77	.96
Dec.	1.38	.88
1906.		
Jan.	1.58	.80
Feb.	1.09	.73
Mar.	1.03	.84

Compared with the uniform curve for nucleation the appearance of the ionization curve is sufficiently distinctive. One might perhaps be inclined to refer the dip in the negative curve between November and February to the more marked "absorption" of the negative ions by the increasing nucleation. But the two curves are not sufficiently similar and there is no reason why the absorbed ion should fail to have a record in the condenser. The only conclusion to be drawn from the results for the distribution of either the positive or the negative ions is this, that there is no discernible relation between the number of ions and the number of Aitken nuclei present in the atmosphere at any time, or that the two distributions result from entirely distinct causes. The ionization of a given region is independent of artificial local contributions, however abundant these may be.

CHAPTER VI.

THE VARIATIONS OF THE COLLOIDAL NUCLEATION OF DUST-FREE AIR IN THE LAPSE OF TIME.

97. Introductory.—Above (Chapter I, section 26, *et seq.*) and in my address* before the Physical Society, I gave an account of observations made several times daily since May 9, 1905, in a search for the possible occurrence of an ultra-mundane radiation. The work was there summarized as follows:

> Using the most sensitive condensation method, *i.e.*, that depending on the depression of the limiting asymptote of non-energized, dust-free air, no change of the quality of scrupulously filtered atmospheric air has thus far been detected. . . . Naturally [ions] would vanish during the slow passage of air through the filter, but fresh ions should be reproduced within the fog chamber by the same agency which generates them without. . . . Probably, therefore, the coronal method is as yet inadequately sensitive to cope with variations of the small nucleations specified.

The ions, which are relatively large nuclei, withdraw much of the available moisture which would otherwise be precipitated on the colloidal nuclei of dust-free air. Hence the size of the terminal corona is diminished. The advantage of the method is its independence of the drop in pressure if this exceeds a certain value.

Since the discovery announced by A. Wood and A. R. Campbell† on the probability of cosmical radiation as evidenced by the existence of a daily period of the same, showing maximum ionization between 8 and 10 A. M. and 10 P. M. and 1 A. M., minimum ionization at about 2 P. M. and 4 A. M., I have taken the subject up again. It seems possible that I overestimated the sensitiveness of the earlier method. I have therefore changed it in the present experiment, replacing the large terminal coronas by the small coronas very near the fog limit.

98. Method and data.—The observations, in other words, are now made with a drop in pressure, but just sufficient to produce coronal condensation on the larger colloidal nuclei of dust-free air ($\delta p = 21$ cm.). The sizes of coronas vary rapidly with the pressure difference and hence with the barometer, p, etc., and great care must be taken with these details. This, however, has been done and the results obtained are given in table 54 and in the chart (fig. 64).

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* Physical Review, XXII, p. 105, 1905; also p. 109, on Radiant fields.

† Nature, vol. 73, p. 583, 1906.

The table gives the angular diameter (s) of the successive coronas, and other data to be presently explained, from which the number of nuclei (n) per cubic centimeter may be obtained. Observations were

TABLE 54.—Colloidal nucleation (s) of dust-free air near the fog limit in their time variations, observed two or more times daily. $\delta p = 27$ cm. (observed at fog chamber, isothermally) $= p - p_3$. Computed $\delta p = p - p_2 = 21$ cm.

Date.	Time.	$p - p_3$.	s.	p.	s^1.	$n \times 10^{-3}$.
1906.	h. m.					
May 21	9 30	27.4	3.6	76.4	3.2	9.7
	12 0	26.7	2.1	....	2.8	6.1
	5 30	27.3	3.0	.3	2.7	5.9
22	9 15	.1	2.9	.7	3.1	8.5
	3 00	.3	3.1	.6	3.0	7.7
23	9 15	.3	2.9	.4	2.7	6.1
	3 15	.5	4.4	.1	3.7	16
24	9 30	.0	2.8	.0	2.8	6.3
	4 00	.1	3.5	75.8	3.2	9.7
25	9 00	.2	4.3	.6	3.8	18
26	8 50	.4	4.9	.4	4.0	19
	3 10	.2	4.9	.3	4.2	22
27	10 25	.1	4.2	.2	3.6	15
	4 25	.1	4.9	.0	4.2	22
28	9 5	27.3	5.2	75.0	4.2	22
	3 45	.1	5.4	74.9	4.6	30
29	11 00	.1	4.9	75.1	4.2	22
	3 50	.1	4.9	.2	4.3	25
30	8 50	.1	2.9	.9	2.7	6
	3 10	.3	3.9	.8	3.3	11
31	9 30	.0	3.0	.9	2.9	7
	2 45	.0	4.5	.6	4.3	25
June 1	9 30	.2	3.9	.7	3.4	12
	2 45	26.9	3.9	....	3.9	17
2	9 5	27.0	3.7	.6	3.5	13
	2 45	.1	3.7	.6	3.3	11
3	10 00	.3	4.9	.9	4.4	26
	4 30	.2	4.2	.9	3.8	18
4	8 30	27.1	3.1	76.4	3.0	8
	3 35	.3	4.3	.2	4.0	19
5	9 20	.1	3.9	75.9	3.7	16
	3 20	.1	4.2	.6	3.8	18
6	10 6	.1	5.0	.1	4.3	24
	3 20	.2	5.9	74.8	4.9	37
7	9 10	.3	4.9	75.6	4.2	22
	3 45	.3	4.8	.9	4.3	25
8	9 25	.1	3.6	76.2	3.6	15
	2 45	.4	4.6	.0	4.0	19
9	9 10	.3	5.0	75.5	4.3	25
	2 45	26.9	3.5	.0	3.1	8
	8 15	27.3	5.1	.1	4.1	20
	9 20	.3	5.1	.3	4.2	22
10	9 55	.2	5.1	.2	4.3	25
	3 15	.3	5.6	.0	4.6	30
	6 15	.2	5.1	.1	4.3	25
11	8 40	.2	4.9	.5	4.3	25
	2 55	.1	4.2	.6	3.8	18

TABLE 54, continued.—Colloidal nucleation (s) of dust-free air near the fog limit in their time variations, observed two or more times daily. $\delta p = 27$ cm. (observed at fog chamber, isothermally) $= p - p_3$. Computed $\delta p = p - p_2 = 21$ cm.

Date.	Time.		$p - p_3$.	s.	p.	s^1.	$n \times 10^{-3}$.
1906.	h.	m.					
June 11	6	5	0.1	3.6	0.8	3.3	11
12	8	45	27.1	3.0	76.3	3.0	8
	12	00	.2	3.4	.3	3.3	11
	3	00	.0	2.8	.2	2.9	7
13	9	00	.1	2.5	.7	2.7	6
	11	40	.1	2.5	.7	2.7	6
	2	35	.2	3.0	.6	3.0	8
	6	5	.2	3.5	.5	3.5	13
14	9	35	.2	3.9	.2	3.7	16
	12	20	.0	2.9	.0	2.9	7
	3	30	.2	4.0	75.8	3.6	15
	6	10	.1	3.7	.7	3.4	12
15	9	20	.1	4.2	.7	3.9	18
	12	00	.2	4.2	.7	3.7	16
	2	40	.1	4.5	.7	4.2	22
	6	00	.1	3.6	.8	3.3	11
16	9	50	.4	4.7	.9	4.1	21
	3	45	.2	4.1	....	3.7	16
17	10	00	.1	4.0	.6	3.6	15
	12	00	.3	5.3	.6	4.6	30
	3	25	.3	5.1	.6	4.5	28
	6	10	26.8	2.8	.7	3.0	8
18	9	15	27.1	3.0	76.0	2.9	7
	12	35	.0	3.0	75.9	2.9	7
	3	00	.2	3.9	.9	3.5	13
	6	00	.2	3.8	.8	3.4	12
19	11	00	.1	3.5	.6	3.1	8
	12	55	.2	4.4	.6	3.8	18
	3	40	.2	4.6	.6	4.0	19
20	5	35	.1	4.1	.7	3.8	18
21	10	15	.3	4.0	.8	3.6	14
	1	00	.1	3.8	.7	3.5	13
	3	10	.1	3.7	.6	3.3	11
	6	20	.1	3.8	....	3.4	12
22	9	15	.1	4.4	.3	3.8	18
	12	10	.1	4.2	.3	3.6	15
	2	50	.2	5.5	.2	4.7	33
	6	10	.2	5.3	....	4.5	28

made at about 9 A. M. and 3 P. M., as near the time of the Wood and Campbell maxima and minima as my duties permitted, on the successive days and hours given by the abscissas.

99. Deductions.—Figure 64 shows in the first place that, in general, minima and maxima of nucleation would have to appear at about the time at which Wood and Campbell observed maxima and minima,

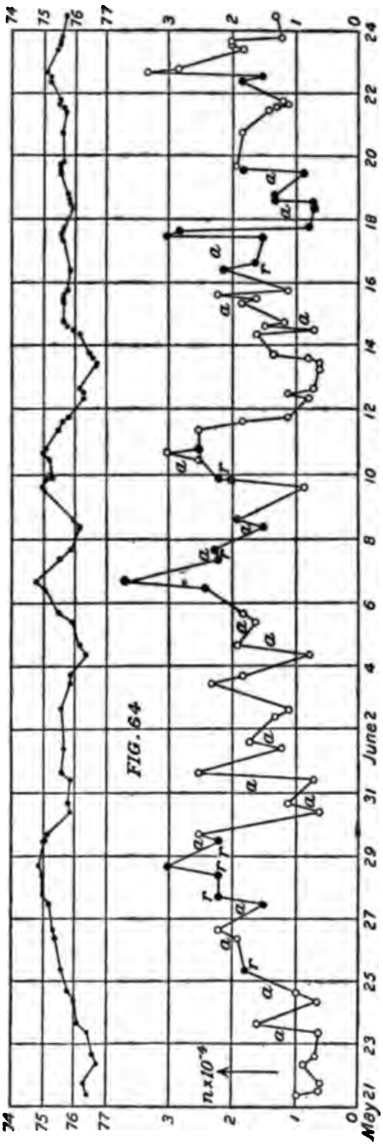

FIG. 64.—Nucleations in ten thousands of colloidal nuclei per cubic centimeter of dust-free air observed on the days and hours given by the abscissas. The branches *a* are in agreement with the Wood-Campbell discovery; the branches *e* show a tendency to inversion; *r* denotes rain. Table 54. Apparatus I. The upper curve (positive downward) shows the initial pressure within the fog chamber and is equivalent to the fluctuations of the barometer.

respectively; or that an inversion of Wood and Campbell's results is a question, since there is usually incremented nucleation in the afternoon as compared with the morning. This, however, may be explained, if the ions are large, even in comparison with the larger gradations of colloidal nuclei. Fewer of these will therefore be captured in proportion as the ionization is larger. Hence the figure shows at *a* an *apparent* corroboration of Wood and Campbell's results; at *e* an omission or inversion of the periods. But the *e*'s are much fewer in number, and in comparison with the amplitude of the *a*'s, the *e*'s are frequently neutral.

In the second place, the high nucleation during the period of rain is noteworthy. Here, then, few ions were present. As there is a modification of the atmospheric potential gradient during this time, one might favor an explanation on similar lines to the ideas suggested by Richardson.*

100. Effect of the barometer.—In the further development of the investigation on the time variations of the efficient colloidal nucleation in filtered air, the results are of the same character as those already discussed; but the dependence of the nucleation on the *fluctuations of the barometer* now shows itself even more obtrusively than before. The minima of atmospheric pressure coincide with maxima of colloidal nucleation, and therefore (by inference but not necessarily) with minima of ionization of the dust-free air, both in the daily and in the weekly periods of observation. Maximum pressure, therefore, would correspond to maximum ionization as if the radiant energy originated in the compression of the atmosphere, or were dependent on the mass of the atmosphere bearing on a given place. This would, if finally substantiated, be an important inference, but no more so than the more direct correlative result that minimum pressure and maximum colloidal nucleation of dust-free air go together.

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* Nature, LXXIII, p. 607, 1906.

At the same time, since the change of absolute temperature (τ) due to a sudden expansion equivalent to a drop (δp) at a barometric pressure (p) and vapor pressure (π) may be written

$$\frac{\tau_2}{\tau_1}=\left(1-\delta p/(p-\pi)\right)^{(k-c)/k}$$

the correction for the changes of the barometer are in the same sense as the observed changes in nucleation. These corrections are found by varying the numerator of $\delta p/(p-\pi)$ and observing the effect on the angular diameter of the corona. While I can see no room for error, it must nevertheless be acknowledged that the present method of small exhaustion, though possibly more sensitive, is not as straightforward as the method mentioned in my address, where no variation could be detected, the terminal corona remaining unchanged.

At the present stage of investigation, therefore, the need of any external radiation has ceased to be obvious; and the results, if they exceed the barometer correction, are most directly referable to changes of pressure within the gas, the number of colloidal nuclei being greatest when the pressure is least.

101. Corrections.—In table 54 and the following table 55, p is the barometric pressure; p_3 the final pressure when fog chamber and vacuum chamber are in communication; p_2 the (computed) pressure which would be observed in the fog chamber if it could be instantly separated from the vacuum chamber after exhaustion. Hence the true drop in pressure is $\delta p=p-p_2$ while $\delta p=p-p_3$ is observed. The initial pressure (p) differs from the atmospheric pressure by a few millimeters, due to the leakage of the 4-inch stopcock from fog chamber to vacuum chamber. As it is impossible to retain the same value of p and δp throughout, a correction must be applied, seeing that the adiabatic cooling is given by $\tau_2/\tau_1=(1-\delta p/(p-\pi))^{(k-c)/k}$, where π is the vapor pressure of water. By varying

δp from 26 to 28 cm. and observing the changes of s (angular coronal diameter) when p is constant, a table was investigated from which reductions could at once be made to $\delta p = 27$ cm. and $p = 76$ cm.; for instance,

$\delta p = 26.8$ cm.	$\delta s = +0.34$	$p = 75.8$	$\delta s = -0.11$
26.9	+ .17	75.9	− .06
27.0	+ .00	76.0	+ .00
27.1	− .15	76.1	+ .06
27.2	− .30	76.2	+ .11

The value of s corrected for both pressures is given in this table.

In the same way the case of apparatus II (to be described presently) was treated, the reductions being much larger here. Thus the data (barometer, 75.5; temperature, 21.4° C.)

$\delta p = 24.9$	$s = 1.7$	$\delta p = 25.6$	$s = 3.1$
25.6	3.6	26.2	5.2
26.4	5.6	25.6	2.9
24.8	1.0		

were consecutively observed, showing that the coronas after long waiting are much larger than when obtained in succession. The efficient nucleation of the fog chamber increases in the lapse of time, probably from the evanescence of water nuclei associated even with small coronas. From these results corrections of the form

$\delta p = 25.5$	$\delta s = +0.27$	$B = 75.9$	$\delta s = -0.08$
25.6	+ .00	76.0	+ .00
25.7	+ .27	76.1	+ .08

were made out. These examples show how critically important these corrections are, and how difficult it will be to decide whether anything more than the barometer fluctuation is being observed.

102. Further data.—It follows from section 101 that there would be a chance for error in the unavoidable leakage of the stopcock, and the best method of coming to a decision would consist in the installation of a second fog chamber, side by side with the other, but containing a smaller exhaust pipe (2 inches in diameter, 18 inches long) and therefore a more perfect stopcock.

Fig. 65 shows two fog chambers (F and F') and appurtenances in place, each with an independent vacuum chamber (V and V') and goniometer. Other parts will be easily recognized.

Table 55 and chart 66 contain the new data, the old fog chamber (4-inch cock) being marked I, the new fog chamber (2-inch cock), marked II. The latter was first tested at different values of δp, and $\delta p = 25.6$

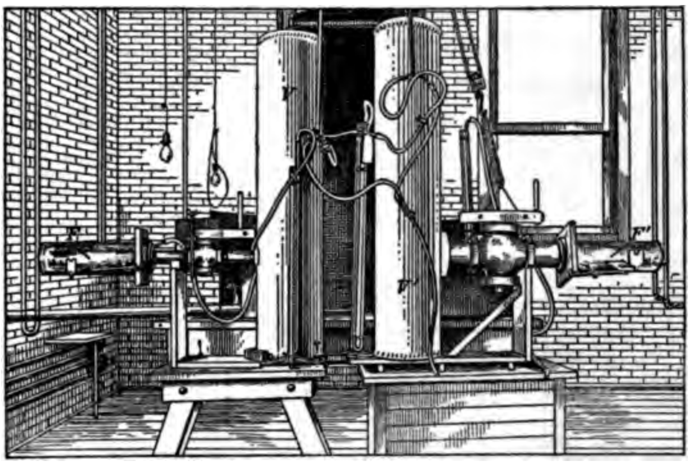

FIG. 65.—Independent fog chambers with 2-inch and 4-inch efflux side by side. Vacuum chambers, V and V'; fog chambers, F and F'.

finally selected. At the outset the values of s may be uncertain, because of internal sources of nucleation and similar difficulties.

Four observations were usually made daily. Data corresponding to I and II are distinguished by subscripts, and those of II were usually observed about five minutes after the time given for I. One may note the much greater efficiency of the apparatus with 2-inch pipes as compared with the other with 4-inch pipes, the reason for which is not easily seen. As a whole the observations for apparatus I during the end of June and the beginning of July run parallel to the barometric decrement, and the astonishingly high values on June 29 and 30 occur during a period

TABLE 55.—Colloidal nucleations near the fog limit in their time variations. Fog chamber I with 4-inch exhaust pipes; $\delta p = p - p_3 = 27$ cm.; II with 2-inch exhaust pipes; $\delta p = p - p_3 = 25.6$ cm.; $p - p_2 = 21$ cm. and 20 cm., respectively.

Date.	Time.		$\delta p_1 = p - p_3$	s_1.	p.	s'_1.	$n \times 10^{-3}$	$\delta p_2 = p - p_3$	s_2.	s'_2.	$n_2 \times 10^{-3}$.
	h.	*m.*									
June 23	9	15	27.1	4.3	75.5	3.8	18	[1]27.6	7.3	6.4	75
	12	35	.1	4.5	.6	4.1	20	.4	7.7	7.4	86
	3	15	.2	4.6	.6	4.1	20	.4	7.3	7.0	82
	5	50	.0	3.6	.6	3.4	12	.3	7.1	7.0	82
24	10	20	.1	3.8	.8	3.5	13	.2	7.5	7.9	93
	12	50	.0	4.1	.7	3.9	18	[2]26.5	5.2	5.0	38
	4	15	.1	3.9	.7	3.6	15	.6	5.1	4.6	30
	6	20	.1	4.3	.7	4.0	19	.5	5.5	5.3	45
25	9	10	.2	5.1	.7	4.6	30	.5	6.0	5.8	57
	12	10	.1	4.0	.8	3.7	16	.5	4.9	4.7	32

[1] Early results.

[2] Results in succession.

TABLE 55.—Continued.

Date.	Time.		$\partial p_1 = p - p_3$	s.	p.	s'_1.	$n \times 10^{-3}$	$\partial p_2 = p - p_3$	s_2.	s'_2.	$n_2 \times 10^{-3}$.
	h.	*m.*									
June 25	3	35	27.1	4.2	75.8	3.9	18	26.5	5.0	4.8	34
	6	10	.1	3.0	.7	2.7	6	.5	5.3	5.1	40
26	9	30	27.1	4.0	76.0	3.9	17	....	...	...	..
	12	20	.1	4.1	75.9	3.9	17	26.5	4.9	4.8	34
	12	35	....	...	.9	...	..	25.6	2.1	2.0	2
	2	40	27.2	5.1	.9	3.7	16	.6	2.6	2.5	4
	5	30	.2	4.7	.9	4.3	25	.6	2.6	2.5	4
27	9	10	.2	4.9	.8	4.5	28	.6	2.7	2.5	4
	12	25	.1	4.9	.7	4.6	32	.6	2.7	2.5	4
	3	00	.1	4.1	.6	3.7	16	.6	3.5	3.2	9
	6	5	.2	4.8	.6	4.2	22	.5	3.5	3.4	11
28	9	5	.3	5.7	.9	5.2	43	.6	3.0	3.0	7
	12	5	.1	4.9	.9	4.7	33	.5	3.0	3.2	9
	3	30	.2	5.1	.8	4.7	33	.5	2.8	2.6	5
29	9	00	.1	5.0	.3	4.5	28	.7	3.7	2.9	7
	12	30	.5	7.0	.2	5.8	59	.6	3.8	3.3	10
	12	40	.2	5.1	.2	4.3	25	....	...	...	..
	2	55	.2	5.4	.2	4.6	30	25.6	3.7	3.2	9
	6	00	.2	5.0	.2	4.2	22	.6	3.8	3.2	9
30	9	25	.5	7.0	.2	5.8	59	.7	4.4	3.6	14
	12	30	.1	5.3	.1	4.6	30	.6	3.2	2.6	5
	3	5	.1	5.3	.2	4.7	33	.6	4.0	3.3	10
	5	50	.1	5.3	.3	4.7	33	.6	4.3	3.7	16
July 1	10	00	27.2	5.1	75.6	4.6	30	25.6	3.3	3.0	7
	12	10	.1	4.5	.6	4.1	20	.6	3.2	2.9	7
	1	45	.1	4.1	.6	3.7	43	.7	3.6	2.9	7
	6	25	.2	5.2	.6	4.7	33	.5	2.9	2.9	7
2	9	15	.4	5.7	.6	4.9	37	.6	3.6	3.3	10
	12	30	.1	4.6	.6	4.2	22	.6	3.6	3.3	10
	2	20	.3	5.5	.5	4.8	36	.6	4.2	3.8	17
	6	00	.2	5.5	.5	4.9	37	.6	3.7	3.3	10
3	9	40	.3	5.6	.5	4.9	37	.6	3.8	3.4	11
	12	30	.2	5.3	.5	4.7	33	.6	3.5	3.1	9
	2	00	.3	5.3	....	4.6	30	.6	3.6	3.2	9
	6	50	.2	5.3	.5	4.6	30	.6	3.9	3.5	13
4	9	15	.2	5.3	.2	4.5	28	.6	4.1	3.5	13
	12	00	.1	5.0	....	4.4	26	.7	4.4	3.5	13
	4	50	.2	5.2	.3	4.5	28	.6	4.3	3.7	16
	6	5	.3	5.2	.5	4.5	28	.6	3.5	3.1	8
5	8	55	.2	4.0	76.5	3.9	18	.6	2.8	3.2	9
	12	10	.4	4.7	.5	4.4	27	....	...	...	..
	2	45	.2	3.7	.5	3.7	16	.6	2.1	3.6	14
	6	20	.2	3.3	.7	3.4	12	.6	1.9	2.4	4
6	9	50	27.2	3.7	77.1	4.0	19	25.6	1.9	2.8	6
	12	35	.1	2.7	.0	3.1	9	.6	1.8	2.6	5
	12	45	.2	2.9	.0	3.1	8	....	...	...	..
	3	15	.2	3.3	76.9	3.5	13	25.6	1.9	2.6	5
	6	10	.3	3.8	.9	3.9	19	.6	1.5	2.2	3
7	9	20	.2	3.6	.7	3.6	15	.6	2.5	3.1	8
	2	25	.2	4.2	....	4.2	22	.0	1.5	3.6	14
	7	45	.2	3.7	76.4	3.5	14	.6	3.5	3.8	17
8	8	50	.2	4.2	.2	3.9	18	.4	2.8	3.5	13
	9	00	.2	3.8	.2	3.6	15	....	...	...	..
	2	55	.2	4.3	.1	4.0	20	.6	2.7	2.8	6
	5	40	.3	4.9	.0	4.4	27	.6	3.0	3.0	7

TABLE 55.—Continued.

Date.	Time.	$\delta p_1 = p - p_3$	s_1.	p.	s'_1.	$n \times 10^{-3}$	$\delta p_2 = p - p_3$	s_2.	s'_2.	$n_2 \times 10^{-3}$.
	h. m.									
July 9	9 00	27.2	5.2	75.8	4.8	35	25.4	3.3	3.5	13
	2 30	.2	5.1	.7	4.6	30	.6	4.1	3.7	16
	5 50	.2	4.8	.6	4.3	25	.6	4.1	3.8	17
10	9 05	.2	5.2	.6	4.7	33	.7	4.0	3.4	11
	2 45	.4	5.7	.5	4.8	35	.6	4.0	3.6	14
	5 45	.2	5.0	....	4.5	29	.4	2.8	3.0	7
11	9 05	.2	4.6	76.2	4.4	27	.5	2.6	3.0	7
	2 15	.2	3.9	.2	3.7	16	....	...	...	...
	5 20	.2	3.9	.2	3.7	16	....	...	...	...

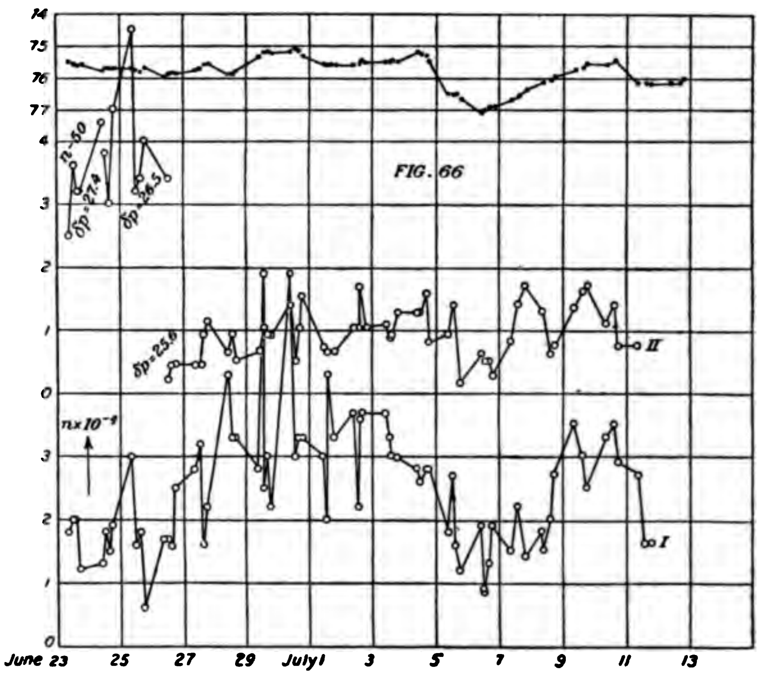

FIG. 66.—Data of fig. 64 continued for apparatus I (fog chamber with 4-inch pipes) and apparatus II (fog chamber with 2-inch pipes), adjusted for different exhaustions ($\delta p = 27.3$ and 25.6 cm., respectively). Table 55.

of exceptionally low barometer. The daily details of the barometer are not as a rule reproduced.

In case of apparatus II, if the initial observations $\delta p = 27.4$ be overlooked, the data for $\delta p = 26.5$ are not unlike magnified parts of the corresponding curve for apparatus I. The chief observations for apparatus II in June ($\delta p = 25.6$ or computed $\delta p = 20$ just above the fog limit) do not in their details, it is true, agree with the curves for apparatus I, except to some degree on June 29 and 30. As a whole, how ever, they also strikingly follow the march of the decrement of the barometer. One may note, moreover, that it is not necessary that the curves for apparatus I and II should quite agree. If, for instance, the preponderating nuclei in the former case are colloidal, and in the latter case ions, one should expect an inverse curve; for the ions in I would decrease the number of efficient nuclei, whereas in II they would increase their number. Decision must be deferred for further observation.

In July the two fog chambers again fail to agree in their daily fluctuations, but both nevertheless follow the barometer closely, in their broader variations. The different sizes of coronas imply different ratios of ions and colloidal nuclei, and hence detailed agreement should not be anticipated. On July 12 the fog chambers were subjected to modifications and it was therefore concluded to terminate the preliminary series of observations at that point, reserving further record and comment for a subsequent report.

103. Conclusion.—It appears, therefore, at the present stage of progress of the investigation on the time variation of the number of larger colloidal nuclei in dust-free wet air, that the meaning of the above results is not quite clear. The probable occurrence of an effect due to anything like cosmical radiation may, however, be regarded as excluded. The nucleation curves vary in their broad contours with the barometer, being a maximum when the atmospheric pressure is least. Nevertheless the two fog chambers do not, in their detailed variation, show appreciable accordance; rather the reverse of this, and yet such a result may be due to differences in the ratios of nuclei and ions entrapped in the differently adjusted chambers. No. II in the above work (Chapter II, section 53) shows apparent excess in the region of ions as compared with No. I. As a whole the data for the time variation can not be regarded as quite trustworthy, since the correction to be added for variation of barometric pressure and the drop of pressure are in the same sense as the residual effect observed. If some obscure factor in the make-up of these corrections has been overlooked, the results may possibly be attributed to it.

From another point of view adequate explanation is now at hand, why in the above investigations it was found impossible to secure reasonably coincident results in the case of those groups of nuclei which lie in the region of the larger colloidal nuclei and of the ions; and it is chiefly for this reason that the results of this chapter are included in the present report.

63

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1907

THE ELECTRICAL CONDUCTIVITY OF AQUEOUS SOLUTIONS

A REPORT

PRESENTED BY

ARTHUR A. NOYES

UPON A

SERIES OF EXPERIMENTAL INVESTIGATIONS

EXECUTED BY

A. A. NOYES, W. D. COOLIDGE, A. C. MELCHER, H. C. COOPER,
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CONTENTS.

PART I. GENERAL OUTLINE OF THE INVESTIGATION. BY ARTHUR A. NOYES.

PART II. ORIGINAL APPARATUS AND METHOD. CONDUCTIVITY AND IONIZATION OF SODIUM AND POTASSIUM CHLORIDES UP TO 306°. BY ARTHUR A. NOYES AND WILLIAM D. COOLIDGE.

1. The conductivity vessel or bomb 9
2. The conductivity measuring apparatus 11
3. The heaters 11
4. Thermometers 13
5. Details of the construction of the bomb 13
6. Procedure for the conductivity measurements 23
7. Procedure for the specific-volume measurements 26
8. Standardization of the apparatus 27
9. Preparation of the substances and solutions 30
10. Discussion of the systematic errors and their correction 30
11. The specific-volume data 35
12. Summary of the specific-volume values 35
13. The conductance-capacity of the apparatus 37
14. The water correction 39
15. The conductivity data 39
16. Summary of the equivalent-conductance values reduced to round temperatures and concentrations 43
17. Change of equivalent conductance with the concentration 48
18. Change of the equivalent conductance with the temperature . . 52
19. Ionization-values and their change with the concentration and temperature 54
20. Summary 53

PART III. LATER MODIFICATIONS OF THE APPARATUS AND METHOD. BY WILLIAM D. COOLIDGE.

21. New material for the shell of the bomb 59
22. Screw-thread on the steel shell 59
23. Special lathe-chuck used in the construction of the bomb 60
24. A new composite lining for the bomb 60
25. A method for removing the lining by hydraulic pressure 61
26. A more delicate leakage test 62
27. Solid platinum-iridium electrodes 62
28. Apparatus and method for rotating the bomb in the heaters . . 64
29. A vapor bath for heating the rotating bomb 66
30. A liquid bath for the rotating bomb 67

PART IV. CONDUCTIVITY AND IONIZATION OF SILVER NITRATE, POTASSIUM SULPHATE, AND BARIUM NITRATE UP TO 306°, AND OF MAGNESIUM SULPHATE UP TO 218°. BY ARTHUR A. NOYES AND ARTHUR C. MELCHER.

31. Outline of the investigation 71
32. Description of the apparatus and method 71
33. Preparation of the substances and solutions 73
34. Systematic errors and their elimination 74
35. The conductance-capacity and the water correction 76

PART IV. CONDUCTIVITY AND IONIZATION OF SILVER NITRATE, ETC.—Continued.

36. Variation of the conductance-capacity with the temperature . . . 78
37. The specific-volume data 80
38. Summary of the specific-volume values 82
39. The conductivity data 83
40. Summary of the equivalent-conductance values 95
41. Equivalent-conductance values at round concentrations 102
42. Change of the equivalent conductance with the concentration . . 104
43. Change of the equivalent conductance with the temperature . . 105
44. Ionization-values and their change with the concentration and temperature 107
45. Summary 110

PART V. CONDUCTIVITY AND IONIZATION OF HYDROCHLORIC ACID, ACETIC ACID, AND SODIUM ACETATE UP TO 218°. HYDROLYSIS OF SODIUM ACETATE AND IONIZATION OF WATER AT 218°. BY ARTHUR A. NOYES AND HERMON C. COOPER.

46. Outline of the investigation 115
47. Apparatus and method of procedure 116
48. Preparation of the substances and solutions 119
49. Systematic errors and their elimination 121
50. Conductance-capacity of the apparatus 124
51. The water correction 125
52. Conductivity data for sodium chloride, hydrochloric acid, acetic acid, and sodium acetate 126
53. Summary of the equivalent-conductance values 133
54. Equivalent-conductance values at round concentrations 137
55. Change of the equivalent conductance with the concentration and temperature 139
56. Ionization-values and their change with the concentration and temperature 141
57. Conductivity data for mixtures of sodium acetate and acetic acid 143
58. Hydrolysis of sodium acetate and ionization of water 143
59. Summary 149

PART VI. CONDUCTIVITY AND IONIZATION OF SODIUM HYDROXIDE UP TO 218° AND OF AMMONIUM HYDROXIDE AND CHLORIDE UP TO 156°. HYDROLYSIS OF AMMONIUM ACETATE AND IONIZATION OF WATER AT 100° AND 156°. BY ARTHUR A. NOYES AND YOGORO KATO.

60. Outline of the investigation 153
61. Apparatus and method of procedure 154
62. Preparation of the substances and solutions 156
63. The conductance-capacity of the apparatus 159
64. The water correction 161
65. Conductivity data for the solutions of sodium hydroxide, ammonium hydroxide, and ammonium chloride 162
66. Summary and discussion of the equivalent-conductance values and their correction to round temperatures 169
67. Equivalent conductance at round concentrations 173
68. Change of the equivalent conductance with the concentration and temperature 175
69. Ionization-values and their change with the concentration and temperature 177
70. Description of the hydrolysis experiments 179
71. Conductivity data for ammonium acetate 179
72. Summary of the specific conductance values 182
73. The hydrolysis of ammonium acetate and the ionization-constant of water 185
74. Summary 189

Part VII. Conductivity and Ionization of Ammonium Hydroxide, Ammonium Chloride, and Acetic Acid at 218° and 306°, and of Sodium Acetate at 306°. Hydrolysis of Ammonium Acetate and Ionization of Water at 218° and 306°. By Robert B. Sosman.

75. Outline of the investigation 193
76. Apparatus and procedure 193
77. Instrumental errors and their corrections 196
78. Preparation of the substances and solutions 197
79. Errors affecting the solutions and their correction 201
80. The specific-volume data 209
81. Conductance-capacity of the apparatus 210
82. The conductivity data 212
83. Equivalent-conductance values at round temperatures 220
84. Final values of the equivalent conductance and their variation with the concentration and temperature 224
85. Ionization-values and their variation with the concentration and temperature 227
86. Hydrolysis of ammonium acetate and ionization of water at 218° and 306° 229
87. Summary 234

Part VIII. Conductivity and Ionization of Hydrochloric, Nitric, and Sulphuric Acids up to 306°, and of Phosphoric Acid and Barium Hydroxide up to 156°. By Arthur A. Noyes and Guy W. Eastman.

88. Outline of the investigation 239
89. Description of the apparatus and method 239
90. Preparation of the substances and solutions 241
91. Discussion of errors and corrections 245
92. Conductance-capacity of the bomb 247
93. The conductivity data 248
94. Summary of the values of the equivalent conductance 256
95. Final values of the equivalent conductance at round concentrations 261
96. Change of the equivalent conductance with the concentration and the temperature 264
97. Ionization of the substances and its change with the concentration and the temperature 267
98. Summary 279

Part IX. Ionization of Water at 0°, 18°, and 25° derived from Conductivity Measurements of the Hydrolysis of the Ammonium Salt of Diketotetrahydrothiazole. By C. W. Kanolt.

99. Outline of the investigation 285
100. Preparation of the substances and solutions 286
101. Apparatus and method 288
102. The conductivity and ionization-constants of ammonium hydroxide and diketotetrahydrothiazole 289
103. Conductivity and hydrolysis of the ammonium salt of diketotetrahydrothiazole 292
104. The ionization of water 296
105. Summary 298

Part X. Solubility of Silver Chloride, Bromide, and Sulphocyanate at 100° By William Böttger.

106. Outline of the investigation 301
107. Description of the experiments 301
108. The conductivity data 305
109. Final conductance values for the saturated solutions 307
110. The solubility values 308

PART XI. THE EQUIVALENT CONDUCTANCE OF THE HYDROGEN-ION DERIVED FROM TRANSFERENCE EXPERIMENTS WITH NITRIC ACID. BY ARTHUR A. NOYES AND YOGORO KATO.

111. Outline of the investigation 313
112. Preparation and standardization of the solutions 314
113. Description of the experiments 316
114. The experimental data 318
115. Summary of the transference numbers 324
116. Summary and discussion 326

PART XII. GENERAL SUMMARY OF THE RESULTS. BY ARTHUR A. NOYES . . . 333

PART I.

GENERAL OUTLINE OF THE INVESTIGATION.

BY ARTHUR A. NOYES.

PART I.

GENERAL OUTLINE OF THE INVESTIGATION.

The investigation to be described in the following series of articles was undertaken for the purpose of studying through a wide range of temperature, extending from 18° to the critical temperature and above, the electrical conductivity of aqueous solutions and such other physical and chemical properties of them as are related to it or can be determined through measurements of it. Aside from its direct physical significance, it is well known that the electrical conductivity of solutions is a property of fundamental importance in connection with the ionic theory; for it gives the simplest and most direct measure of the ionization of substances, upon which their chemical behavior in solution depends. A full investigation of this property at all temperatures would therefore furnish a comprehensive knowledge of the chemical equilibrium of dissolved substances in water; and if supplemented by determinations of the solubility of solid salts, which determinations can also be made by measuring the conductance of their saturated solutions, a fairly complete basis for the development of the chemistry of aqueous solutions of electrolytes would be obtained.

A large number of such investigations had previously been carried out at ordinary temperatures, especially at 0°, 18°, and 25°, and a few of them had been extended to somewhat higher temperatures; yet even at 100°, where the results have much practical importance owing to the frequent use of boiling solutions and owing to the fact that it is the limiting temperature attainable in open vessels, few, if any, accurate data had been obtained owing to the difficulties arising from evaporation and from contamination when glass vessels are used. This temperature has therefore been selected in this investigation as one of those at which each substance will be studied. Above 100° only a few isolated conductivity measurements have been published.* Yet the solubility of substances and their chemical condition in solution at these higher temperatures is of much importance, not only from the standpoint of physical and chemical science, but also from that of chemical geology and the chemical technology of reactions under pressure.

---

*Thus Sack (Wied. Ann., **43**, 212-224, 1891) investigated the conductivity of three copper sulphate solutions up to 120°. Maltby (Z. phys. Chem., **18**, 155. 1895) found that upon heating up to 237° the conductance of an aqueous potassium chloride solution steadily diminished. Hagenbach (Drude's Ann., **5**, 276-312. 1901) observed a maximum in the equivalent conductance of a 0.01 normal KCl solution. In all of these experiments the conductivity cell was made of glass and was necessarily very small; therefore, owing to the solubility of glass at these temperatures and to the danger of polarization of the small electrodes used, the results have little significance.

It was not, however, primarily the direct value, however great, of the physical and chemical constants of specific substances at high temperatures that led to this investigation, but rather the hope that, by determining them under widely varied conditions of temperature and pressure, general principles might be established relating to the influence of these factors on the migration-velocity of ions, on the ionization of dissolved substances of different types and of water itself, on the hydrolytic dissociation of salts of weak acids or bases, and on the solubility of substances, and that relations might be shown to exist between some of these properties and other properties of the solvent, such as its density, viscosity, and dielectric constant. Additional light might also be thrown on the cause of the complete divergence of the change in the ionization of largely ionized compounds with the concentration from the requirements of the mass-action law* — a divergence which constitutes one of the most serious imperfections of the theory of solutions, and which may well conceal a discovery of great importance.

The first and most difficult part of this research consisted in the construction of a conductivity vessel composed internally of material unacted upon by aqueous solutions and capable of withstanding without leakage the high vapor-pressure of such solutions up to the critical temperature. This portion of the work was carried out by Dr. W. D. Coolidge. After three years' continuous work upon this problem, the mechanical difficulties were overcome and a platinum-lined bomb with insulated electrodes was constructed which remains perfectly tight at any rate up to 306°, which occasions only an unimportant contamination even in salt solutions as dilute as $\frac{1}{1000}$ normal, which yields conductivity measurements accurate to 0.2 per cent, or less, and which at the same time makes possible specific-volume determinations, which are essential to the interpretation of the results. Now that a knowledge of the necessary mechanical devices has been acquired, the making of such a bomb is an easy task for a skilled instrument-maker. Therefore, in Part II of this publication will be first described in full detail, with the help of working drawings, the apparatus used in the first measurements, and especially the construction of the bomb, in order to make it readily available for investigators who desire to pursue researches of the same kind or those requiring similar apparatus (such, for example, as a calorimetric bomb). This description, together with the results with sodium and potassium chlorides referred to in the next paragraph, was published in November, 1903, in the Proceedings of the American Academy of Arts and Sciences.† It is reproduced here, in

---

*For a brief general discussion of this matter, see Noyes, Congress of Arts and Sciences, **4**, 311-323 (1904); Science, **20**, 577-587 (1904); reviewed in Z. phys. Chem., **52**, 634-636 (1905).

†Proc. Am. Acad., **39**, 161-219 (1903). Also in Z. phys. Chem., **46**, 323-378, and in somewhat abbreviated form in J. Am. Chem. Soc., **26**, 134-170.

somewhat revised form, for the sake of completeness and on account of its close relation to the new material that is to be presented.

I desire in this connection to express my great indebtedness to the American Academy for the liberal grants made to me from the Rumford Fund in the early stages of the work.

During the past four years the work has been continued under the auspices of the Carnegie Institution of Washington, and its progress has been largely due to the assistance thus afforded. I have also been fortunate in having had associated with me a number of able research workers, by whom the work has been prosecuted on its different sides.

With this apparatus and method in its original form, conductance and specific-volume measurements were made by Dr. W. D. Coolidge and myself with two substances, sodium and potassium chlorides, at various temperatures between 26° and 306° and at various concentrations between 0.1 and 0.0005 normal. The results of these experiments are also presented in Part II. Since their original publication several corrections of a minor character have been applied to the data.

As was to be expected a number of important improvements in the apparatus and method suggested themselves in the course of these experiments, and these were subsequently worked out by Dr. Coolidge, who presents a description of them for the first time in Part III of this publication. The method is now being further developed so as to adapt it to still higher temperatures extending above the critical one, where a control of the pressure, entire elimination of the vapor space in the bomb, and measurements at small intervals of temperature will be essential.

Mr. A. C. Melcher has made measurements with another salt of the uni-univalent di-ionic type (silver nitrate), and has then extended the investigation to salts of other types (potassium sulphate, barium nitrate, and magnesium sulphate), at a series of temperatures up to 306°, namely, 18°, 100°, 156°, 218°, 281°, and 306°. The results of these experiments, as well as some additional ones with sodium and potassium chlorides, are presented in Part IV.

Dr. H. C. Cooper, Mr. Yogoro Kato, and Mr. R. B. Sosman have studied the conductivity and ionization up to 218° of certain acids and bases; namely, of hydrochloric and acetic acids and of sodium and ammonium hydroxides. They have also determined by conductivity measurements the hydrolysis of sodium acetate at 218° and that of ammonium acetate at 100°, 156°, and 218°, and have calculated therefrom at these temperatures the ionization-constant of water itself, upon which in large measure the phenomenon of hydrolysis depends. This work is described in Parts V, VI, and VII; the share of each investigator being indicated under the separate titles of these parts. Mr. R. B. Sosman has made an entirely similar series of measurements at 306° with ammonium hydroxide, acetic acid, and ammonium acetate, and has derived from them the ionization of water at that temperature. The results are also presented in Part VII.

Mr. G. W. Eastman has investigated a number of other acids, namely, nitric, phosphoric, and sulphuric acids, and potassium hydrogen sulphate, and the base, barium hydroxide, at 25° or 28° intervals from 18° to 156°, and has extended some of these measurements and the previous ones with hydrochloric acid to 260° and 306°. The data and conclusions in regard to these substances are presented in Part VIII.

In order to obtain at temperatures of 0° to 25° values for the ionization of water more accurate than those previously existing, Dr. C. W. Kanolt has studied by the same conductivity method as was used with ammonium acetate at higher temperatures the hydrolysis of an ammonium salt of a much weaker acid, diketotetrahydrothiazole. The results of this work are presented in Part IX.

Only a beginning has been made in the study of the solubility of salts at high temperatures. Dr. Wilhelm Böttger has, however, already determined that of three difficultly soluble silver salts at 100°, and the results are recorded in Part X.

It has also seemed advisable to include in this publication an account of a research carried out by Mr. Yogoro Kato and myself with the view of determining the equivalent conductance of the hydrogen ion; for though this consisted in transference experiments at 20° with nitric acid of various concentrations, and was thus distinct as far as the method is concerned from the other researches to be here described, yet the knowledge furnished by it has a direct bearing on the interpretation of conductivity results. The investigation is described in Part XI. It is entirely analogous to one previously made with hydrochloric acid by Noyes and Sammet* for the same purpose.

Finally a general summary and discussion of the more important results of the whole series of investigations are presented in Part XII.

The reader who is interested only in the more general conclusions drawn from the work is recommended to turn at once to this summary in Part XII. Anyone who desires fuller information in regard to the conductivity and ionization of the specific substances and to the method of discussion of the results will find this information as a rule in the last five or six sections of the separate parts. The earlier sections in each part are devoted to a detailed description of the experiments and presentation of the original data, and will be of interest principally to investigators who desire to make similar experiments and to those who wish to criticize the results or form an estimate of their accuracy.

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*The Equivalent Conductivity of the Hydrogen Ion derived from Transference Experiments with Hydrochloric Acid. J. Am. Chem. Soc., **24**, 944-968 (1902), or Z. phys. Chem., **43**, 49-74 (1903).

PART II.

ORIGINAL APPARATUS AND METHOD. CONDUCTIVITY AND IONIZATION OF SODIUM AND POTASSIUM CHLORIDES UP TO 306°.

BY ARTHUR A. NOYES AND WILLIAM D. COOLIDGE.

PART II.

ORIGINAL APPARATUS AND METHOD. CONDUCTIVITY AND IONIZATION OF SODIUM AND POTASSIUM CHLORIDES UP TO 306°.

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1. THE CONDUCTIVITY VESSEL OR BOMB.

A vertical section of the conductivity vessel used throughout these investigations is shown in half size in fig. 1. It is a cylindrical vessel *A*, with a cover *B*, which is held in place by the large nut *C*. *A*, *B*, and *C* are made of soft crucible steel. To prevent contamination, the bomb is lined throughout with sheet platinum 0.41 mm. thick. The cover joint is made tight by a little packing ring, made of pure gold wire, which fits into a shallow V-shaped groove. As may be seen in the diagram, the platinum lining, indicated by a heavy line, goes under this ring and a little distance beyond it, the outer edge being fastened to the shell by eight small steel screws, of which two are shown. The lower vessel has a capacity of about 122 c.cm.

The body of the bomb serves as one electrode, connection being made with it by means of the large binding post on top of the nut *C*. The second electrode is brought in through the bottom of the bomb and is insulated from the latter by means of the mica washer *M*, the air space *S*, and the quartz-crystal piece *Q*. The body of this electrode is of steel, but its upper part is covered with sheet platinum. On the bottom of the crystal piece is turned a single sharp V-shaped ridge, and this rests on a flat gold washer which is inserted between the crystal and the bottom of the bomb. Another gold washer is placed between the upper part of the electrode and a second V-shaped ridge turned on the upper face of the crystal. The nut *N* fitting on the lower, threaded end of the electrode, draws the latter down, thus forcing the ridges of the crystal into the soft gold and making the joints tight. *Z* is a brass washer which by its greater expansion-coefficient makes up for the difference in the expansion, upon heating, of the quartz-crystal and of that part of the steel electrode which lies within. The second nut, on the lower end of the electrode, serves to bolt on a small copper tag to which the wire L_2 is silver-soldered. The quartz piece *Q* is extended in the form of a cup above the electrode, so as to increase the resistance-capacity of the cell.

In the cover *B* is a narrow cylindrical chamber provided with an "auxiliary electrode," which is insulated in just the same way as the lower electrode. The purpose of this small chamber with the auxiliary electrode is twofold: first, it serves as a safety device, showing that the bomb has not become completely full of liquid; and secondly, it furnishes a means of measuring the specific volume of the solutions. The first provision is necessary since the bomb is designed to withstand the vapor pressure, but not the fluid pressure of the liquid. A knowledge of the specific volume is required in order to calculate the equivalent from the observed conductance. A measurement of the resistance between L_1 and L_3, together with a measurement of that between L_1 and L_2, when preceded by a calibration which may be made once for all, shows, as will be explained more fully in section 8, at any time after the solution has expanded sufficiently to come into contact with the auxiliary electrode, just how high the liquid stands, and therefore how much vapor space remains.

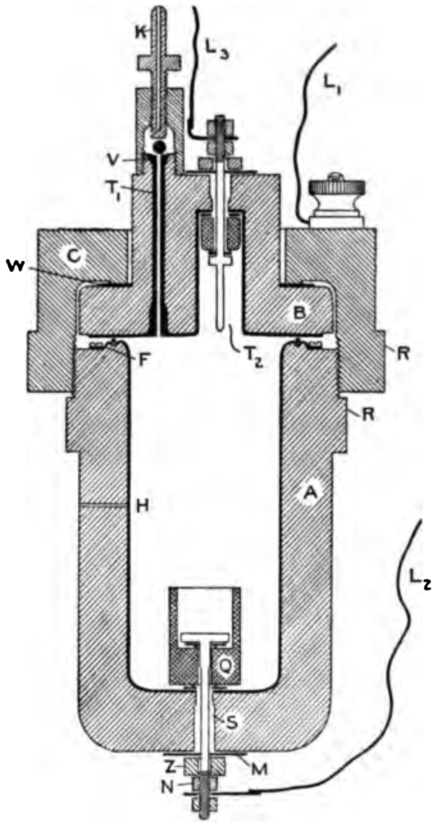

Fig. 1.

The small platinum tube T_1 serves to exhaust the air from the bomb. The method of doing this will be apparent from the diagram and the following description. The hollow screw K is connected by means of rubber tubing with a Richards water pump, and is at first raised so that air can come out under the little steel bicycle ball which rests on the upper end of the platinum tube. After the air is removed until a pressure gauge shows a pressure within of about 2 cm., and while the pump is still in operation, the part K is screwed down, thus forcing the steel ball upon its seat and closing the end of the tube.

The solution comes into contact with nothing but platinum, quartz-crystal, and gold, except at the top of the narrow tube, T_1, where it may touch the steel ball. The latter could be gold-plated; but this has proved unnecessary, since there is scarcely any circulation through the narrow tube.

The lower electrode, as well as the auxiliary electrode and its surrounding tube, are well platinized. The body of the lining is not platinized, since on account of its great surface this is not necessary.

2. THE CONDUCTIVITY MEASURING APPARATUS.

The conductance was measured by the ordinary Kohlrausch-Wheatstone bridge method, using the induction coil and telephone. The slide wire was of platinum-iridium; it was 1 meter in length and 0.4 mm. in diameter. The resistance coils, 2,000 ohms in all (or 4,000 ohms in a few measurements), were of manganine. The whole conductivity apparatus was mounted on a small portable table so that it could be moved about as the bomb was changed from one heating bath to another. It was always kept at a distance from the heaters. No temperature correction needed to be applied to the resistance coils. Heavy flexible copper leads were used up to within a few centimeters of the top of the heaters, where they were joined by means of brass connectors to the smaller copper wires, L_1, L_2, L_3, coming from the bomb. A double-throw switch served to connect the conductivity apparatus with L_1 and L_2 or with L_1 and L_3.

3. THE HEATERS.

Conductance measurements were made at about 26°, 140°, 218°, 281°, and 306°. The first of these temperatures was attained by immersing the bomb in a bath of commercial xylene contained in a double-walled, well-jacketed, metal cylinder. This substance has the advantages that it is a good insulator, non-corrosive, and not very volatile, and that the bomb can be transferred from it directly, without cleaning, into the xylene-vapor bath by which the next higher temperature is attained. The liquid was stirred by a small propeller, and was heated electrically at will with the help of a platinum helix immersed in it.

For all the higher temperatures, vapor baths were employed, as these furnish the only safe and rapid method of heating. The temperature adjusts itself automatically, and can never rise much above the ordinary boiling-point, thus giving protection against overheating and undue expansion of the liquid within the bomb, which by completely filling it might cause it to burst. Moreover, if the bomb should spring a leak, it would be dangerous in the case of a liquid bath; for the steam, escaping under such pressure, might throw some of the hot liquid upon the observer. Steam leaking out into the hot vapor, on the other hand, causes no annoyance further than that arising from the odor of the vapor and the loss of the material in the case of the expensive substances. An air bath would, of course, not be open to this objection; but the heating would be extremely slow and non-automatic.

An elevation of one of the heaters — all of which were substantially alike — with the bomb in place is presented in fig. 2. The bath is made of a piece of wrought-iron pipe *A*, 16 cm. in diameter and 40 cm. long, with a bottom piece welded in. Near the top two pieces of iron pipe *C* about 2 cm. in diameter and 25 cm. long are screwed in, to serve as condensers. These condenser tubes are given a slight pitch, but their outer ends should not be higher than the top of the heater. To increase their efficiency, a loose roll of iron-wire gauze is put into each of them. The top of the bath, which should be turned off square in the lathe, is covered with a large watch-glass *D,* in which holes are drilled for the thermometer *T,* and the lead-wires to the bomb. A tube of thin sheet iron *Q,* about 12 cm. in diameter, with a flange at the bottom, is placed in the heater and held in the middle by projecting pins. Small holes are drilled through this tube at the bottom, and two rows of large holes at the top. The function of this tube is to prevent the bottom of the bomb from getting hotter than the top; for, if it does this by ever so little, a constant evaporation and condensation goes on in the bomb, which interferes with the readings of the auxiliary electrode and the specific-volume determinations. The inverted mica cone *N* is put in for the same purpose; it prevents the cold condensed vapor from dripping upon the top of the bomb. These arrangements also protect the bomb more effectually from radiation and convection-currents from the walls of the heater. The holes in the glass cover through which the lead-wires and the thermometer enter are but little larger than these, so as to prevent loss of vapor. The thermometer is supported by means of a cork stopper which rests on the top of the watch-glass. The insertion of cork stoppers in the holes is not advisable, as they cause the hot liquid to escape through their pores. The bomb is supported in the heater by means of a brass frame *F,* and suspension wires *W,* which hang on two steel pins screwed into the walls of the heater. At the top of each of the two suspension wires is a loop, so that by inserting a steel hook in each of these loops, the bomb is easily removed from the bath while still hot. The sides of the heater are well jacketed with asbestos. It is supported on a metal tripod by means of three steel pins, which project through the asbestos covering. It is heated by gas-burners below, one sufficing after the bomb and heater have become hot.

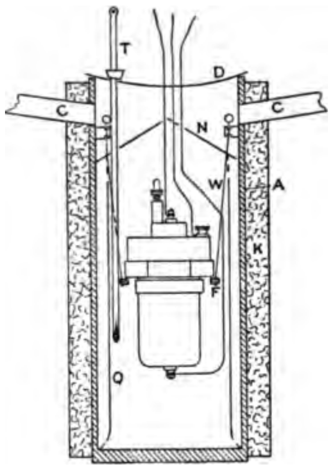

Fig. 2.

Commercial xylene was first used for the 140° bath, but the pure meta-xylene was found to give a more constant temperature and one more uniform in the upper and lower parts of the bomb. To prevent the escape of the vapor, it was necessary in this case to cause water to circulate through a jacket surrounding one of the condenser tubes. Pure naphthalene from Kahlbaum was used to give a temperature of 218°, and was found to be an ideal substance. α-Bromnaphthalene was employed for the next higher temperature (281°), as it seemed to be the only available substance; it is not convenient, however, since it decomposes slowly upon boiling with formation of tar and hydrobromic acid (which attacks the outside of the bomb); it must therefore be frequently removed from the heater and redistilled. The highest temperature (306°) was maintained with benzophenone, which shows no change of boiling-point even after many days of continuous heating.

4. THERMOMETERS.

The temperature of the liquid xylene bath was measured with an ordinary thermometer reading directly to tenths of a degree, and this was checked from time to time against a standard Tonnelot thermometer.

For the higher temperatures French mercurial thermometers, made by Alvergniat, with a range of 360° and graduation in degrees, were used. By the use of a little reading telescope these thermometers were read with certainty to 0.1°. They were standardized as described in section 8 of this article. The mercury column was always completely immersed in the vapor, and to take a reading the thermometer was quickly raised only enough to render the meniscus visible above the top of the heater. Repeated trials showed that the temperature of the bath throughout the space surrounding the bomb varied less than 0.1°, so that the exact position of the thermometer made no difference. Care had to be taken, however, that the mica shield above the bomb did not come in contact with the thermometer stem, thus allowing the condensed vapor coming from the shield to run down and cool the bulb. It was feared that the vapor condensing on the upper part of the thermometer itself would have the same effect; but this was proved not to be the case by fastening a small inverted watch-glass about midway on the thermometer stem; this carried off the drip from the upper part of the stem, but did not affect the reading.

5. DETAILS OF THE CONSTRUCTION OF THE BOMB.

The shell is made of the softest crucible steel obtainable, ductility being desired rather than high tensile strength. Extra weight is not objectionable here, as it would be in the case of a calorimetric bomb; moreover, fear was entertained that a high-carbon steel might be weakened by the repeated heating and cooling to which the bomb was to be subjected. The shell was designed for approximately equal strength throughout. The large nut *C* has an ordinary V-shaped thread of 18 turns to the inch. To tighten the nut, the lower part of the bomb is held at *R*, which is hexagonal, by a wrench bolted to a firm table; while a second wrench, with an effective length of 46 cm., is placed on the hexagonal part *R'* of the nut itself. In this way sufficient pressure can be exerted on the gold packing-ring to make the metal of which it is composed actually flow into the groove beneath, filling any little scratches or other depressions which may exist in the latter. Since there is a certain thickness of gold and platinum interposed between the cover and the lower part of the bomb, and since these both expand less than steel upon heating, it becomes necessary to use a compensating brass washer *W* between the nut and the cover. The proper thickness can be calculated from the known coefficients of expansion of the three metals. Care must be taken that the bearing surface of the nut *C* on the washer *W* is so large that the upward force of the steam acting on the cover does not compress the brass washer, and thus allow the cover to rise. Care must also be taken — and this is very important — that the distance from the center of this bearing surface to the axis of the bomb is less than the radius of the gold packing-ring; otherwise the cover might turn on the ring while the nut was being tightened, which would prevent a tight joint from being secured. For lubrication a little finely powdered graphite is rubbed on the top of the brass washer and into the threads of the large nut.

To facilitate the removal of the platinum lining, the inside of the steel shell was made slightly tapering (about 0.05 mm. in 10 cm.), and the little grooves left by the boring tool were carefully ground out.

In working with the bomb it proved to be necessary to drill through the steel shell a number of small holes, one of which is shown at *H* in fig. 1. In the present bomb there are about 75 of these (probably half as many would have sufficed) well distributed over all its parts, *A, B,* and *C*. These holes are 0.66 mm. in diameter — so small that they do not seriously weaken the shell, and that the platinum lining is capable of withstanding the pressure over their areas. These holes are made necessary by the fact that without them some water gets trapped between the lining and the shell, owing to slight leakage or permeation of the platinum itself when the bomb is first heated, the lining then being not in close contact with the shell at every point; and this water on subsequent heating exerts, owing to its expansion in the liquid state, an enormous pressure against the lining, causing little indentations in it and causing some water to flow back into the bomb, whereby contamination of the solution with iron is produced. The holes remedy entirely this difficulty, which otherwise will become aggravated on each successive heating. They also help to locate a leak in case one exists, for when the bomb is connected to the hydraulic pump to be tested, as will be explained later, they permit the water to escape at a point near where it gets through the platinum lining. To further this end a small hole is also drilled from the outside obliquely into the air space around each of the electrode rods.

The lining of the lower part of the bomb *A* was made of a platinum-iridium alloy (2 per cent iridium) 0.40 mm. thick. The flange *F* was originally made of the same material, but the closing of the bomb compressed the platinum each time under the ring so that it grew hard and thin and finally cracked at the bottom of the groove. For this reason platinum-iridium alloy containing 15 per cent iridium had to be substituted for the flange. This is so hard that it bids fair to wear indefinitely, and yet it is not so brittle that it can not be forced into the groove in the steel without cracking. The flange could just as well be welded to the platinum cup, but in our bomb it was soldered to it with pure gold. Pure gold was also used freely in making repairs on the present lining when it tore, as it frequently did at the start, before the necessity of the small holes in the shell and of several other precautions was understood.

The lining is made so as to fit as well as possible at the start. It is then inserted in the shell, and expanded by driving in plugs of cotton as hard as possible, with a hammer and piece of hard wood. The shell is then placed in the lathe, and the lining is still further expanded by the use of an agate burnisher lubricated with soap. The flange is next hammered over to fit the steel, sheet lead being used under the hammer to prevent injury to the platinum alloy. The most delicate operation connected with the lining of the bomb is perhaps the next step, which consists in making a depression in the flange to fit the V-shaped groove in the steel below. This groove in the steel should not be sharp as shown in fig. 1, but should be slightly rounded at the bottom (to prevent cracking the hard flange) and its sides should make an angle of 90° with one another. The depth of the groove is such that when a wire 0.8 mm. in diameter is laid in it, about one-half of the wire lies outside the groove. A little steel roller is made to fit the groove in the shell, and this roller, after being hardened and polished, is pivoted in a fork which fits into the tool post of the lathe. The shell with the lining in it is then slowly rotated in the lathe while the roller, well lubricated with soap, is firmly pressed against the flange over the groove.

After the lining has been made to fit as closely as possible, it should be removed from the shell and heated to redness to anneal it. Even the flange had better be treated in this way, since it is hard enough even after annealing. To remove the lining after it has been fitted in in the preceding manner, the following plan was adopted: Take a stick of soft wood, perhaps 20 cm. long and 5 cm. square, and whittle one end down so that it will slip easily into the bomb. Then take a piece of cotton cloth moistened with alcohol to remove any grease, wrap it over the small end of the stick, and then with a hammer drive the latter tightly into the bomb. Now holding the bomb in the vise, grasp the projecting end of the stick firmly in the hands or in a wooden clamp and twist out the lining. This method never fails, provided the steel shell was ground reasonably smooth at the start.

A hole is drilled in the lining at the bottom so as to correspond with the hole in the steel shell. It is then best to close this hole temporarily with the steel piece shown in fig. 3, using a lead washer under the **V**-shaped ridge for packing. Then, in order to bring the lining into perfect contact with the shell and at the same time to test it for possible faults, the lower part of the bomb is connected by means of the auxiliary cover shown in figure 4 with a Cailletet pump or its equivalent — a water reservoir being interposed between the pump and the bomb so as to force water instead of oil into the bomb. For this testing of the lining a pressure of 300 atmospheres has been used, the steel shell having previously been similarly tested up to 600 atmospheres pressure. The lining must be fitted as closely as possible before the hydraulic pressure is applied, since otherwise this will always result in tearing the lining. Even after expanding the lining with hydraulic pressure, there is no trouble in removing it, in case a leak develops, by the method given above.

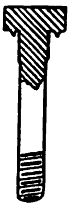

Fig. 3.

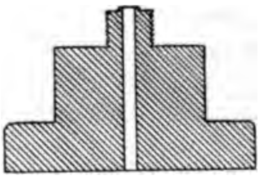

Fig. 4.

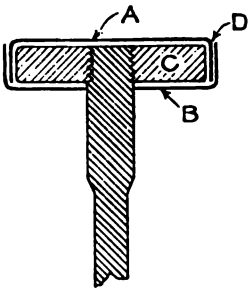

Fig. 5.

The next step is to fasten the edge of the flange to the shell. If this is not done, when substances like benzophenone, solid at ordinary temperature, are employed for heating the bomb, they will be drawn under the flange and into the groove in the shell, where they will solidify; upon heating the bomb the next time, the solid melts and escapes, thus relieving the pressure on the packing-ring and allowing the bomb to leak; moreover, if the edge is not fastened down, there is danger of bending it when the bomb is opened and handled. To secure the flange eight small steel screws are used. The steel shell has to be recessed at this place, as shown in fig. 1; otherwise the screw heads would interfere with the cover.

The lower electrode is made of two steel parts, as shown in fig. 5, the horizontal part *C* being afterwards inclosed in a platinum box, which is made as follows: The top *A* of this box, is made by forcing a circular disk of pure sheet platinum (about 0.25 mm. thick) through a brass die by means of a brass punch. It is better, since it strains the platinum less, to interrupt this operation at least twice, annealing the metal each time. This box should be made to fit so tightly over *C* that it has to be forced on. In the same way a tight-fitting bottom *B* is made for this box. A hole is drilled in the center of this just large enough to permit the passage of the steel rod through it. It is then forced on over *A*. It then remains only to solder *B* to *A* with pure gold. This is easily accomplished by putting several pieces of gold on the crack *D* and directing a hot flame from the blast lamp downwards upon the box. This flame must not be too small, since the whole of the soldering must be done at once and as quickly as possible. Doing it a piece at a time involves keeping the steel rod hot for a longer time, and consequently oxidizing it more; and worse than this, the gold gets inside and alloys with the iron, bringing the latter eventually to the surface. Before soldering it is better to cover the steel rod below the box with pieces of asbestos, binding them on tightly by means of a wire, so as to diminish the oxidation.

Before adopting quartz crystal as the insulator various other substances were tried. Mica was tried first of all, using both of the methods subsequently employed by Knipp* in his work on surface tension. Our experience agreed with his — that it is impossible to secure an absolutely tight joint with mica because of the formation of radial cracks. Nor was it an ideal substance chemically. Carnelian, flint, and agate were next tried because of their known toughness. It was with the last-named substance that we developed the method finally employed for making an absolutely tight joint; the substance itself, however, proved to be chemically unsuitable, since the hydrated silica which it contains dissolves readily in the hot water. The method which we finally employed for securing a tight joint put very little strain on the agate, so that there was no longer any reason for avoiding a substance because of its brittleness. Quartz crystal was then the natural substance to try. Japanese quartz, however, proved a failure, owing to included water or carbon dioxide, which caused it to crack upon heating; but the Arkansas quartz which we next tried was not affected by heat and has proved to be very satisfactory. Since the thermal coefficient of expansion is so different in the directions parallel to and perpendicular to the main axis of the crystal, the axis of the cup was made parallel to the main axis of the crystal.

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*Phys. Rev., **11**, 129-154 (1900).

The process employed for making the quartz cup is as follows: A crystal is selected which is perfectly clear and free from imperfections. A slice, in thickness a little greater than the height of the finished cup, is then sawed out at right angles to the main axis. For this operation a thin tinned-iron disk, whose edge is charged with diamond powder, is rotated in the lathe; and the piece, supported on a sawing table, is pressed lightly against the saw by hand, a wet sponge being held against the edge of the saw with the other hand. This operation of sawing is discussed at some length by Threlfall.* It is both easy and rapid if the saw is in good condition. Care must be taken in this and the subsequent operations that the work is not crowded too hard against the abrading surface, as this causes a local rise of temperature which may crack the crystal. A hollow drill, whose internal diameter is but little greater than the external diameter of the finished cup, is then run through the crystal piece at right angles to the sawed surfaces. Such a drill consists merely of a tinned-iron tube provided with a slit running lengthwise, and mounted so that it can be rotated in the lathe. The outer end of the tube is turned off square and is then charged with diamond powder. A small piece of wet sponge is then placed in the tube. Powdered carborundum can be used in place of diamond, and, although it is somewhat slower in starting, it appears to be equally satisfactory afterwards. The core is then taken from the drill and the ends of the cylinder are ground down flat; for the saw has left them somewhat irregular. This operation of grinding is conveniently carried out by means of a carborundum wheel rotated in the lathe, the wheel being kept wet by holding a sponge against it. Before grinding either surface, its bounding edges must be ground off (beveled); otherwise the edges will break out irregularly. To cup out the cylinder, a hollow drill, whose external diameter is but little less than the internal diameter of the finished cup, is then run into one end to a depth almost equal to that of the desired cavity. The core which is left from this drill is too strong to be broken out without danger of injuring the outside of the cup; so another, smaller one is next run in to the same depth as the first and concentrically with it. This leaves two fragile pieces, a small rod and a thin tube, which are easily broken out. The cup is next mounted so that it can be rotated in the lathe. This is best accomplished by fastening it with stick shellac to the end of a brass rod held in the lathe chuck. To hold firmly, the crystal must be heated above the melting-point of the shellac; this can be done safely by flashing it with a gas flame. The inside of the cup is then ground to its final diameter and the bottom made flat by using carborundum powder upon the end of a brass rod which is a little less in diameter than the cavity and whose end is squared off, the rod being best held in the hand. The small hole is drilled through the bottom of the cup by the aid of a small diamond set in the end of a steel or brass rod. The diamond must, of course, be a little larger than the rod to give clearance for the latter. To start the hole the **T**-rest is used, but afterwards the rod is supported only by the hand. The tool must be withdrawn and moistened very frequently. The hole may be run half-way through from either end. It is afterwards expanded to its proper size by the aid of a small brass or steel rod and some carborundum. To form the little **V**-shaped ridges on the ends of the cup, each of the end surfaces, except at the middle where the ridge is to be, is ground down with carborundum. The projecting portion left in the center is then turned into a sharp ridge by means of a diamond set in the end of a steel rod. This tool is held in the hand and supported on the **T**-rest just as the ordinary hand tool is used on metal. To support the cup while work is being done on the lower end it is best to fasten in the chuck a piece of brass rod somewhat smaller than the internal diameter of the cup, square off its end, turn a little groove in it which will correspond to the ridge at the bottom of the cup, and then shellac the cup on, so that the ridge comes in the groove. This mode of support insures getting the ridges, as they should be, in parallel planes and centrally located with reference to the axis of the cup. The operation of polishing is best carried out by means of different grades of corundum powder, using finally oxide of tin. These are applied wet on the end of a soft piece of wood.

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*On Laboratory Arts, pp. 187-189.

In making such a cup an ordinary mechanician, after a little practice on the different operations, will spend perhaps twelve or fifteen hours.

The thickness of the brass compensating washer (*Z*, fig. 1) can be calculated from the known coefficients of expansion of the quartz-crystal and of the brass and steel used. That used in our bomb was 5.1 mm. in thickness. Of the two gold washers the upper one is made to fit tightly on the electrode rod, while the hole in the lower one is made to correspond with that in the bottom of the bomb. To keep the lower gold washer from touching the electrode rod, and to keep the latter from touching the steel shell, the following device was employed: The middle part of the steel rod is made about 0.5 mm. smaller in diameter than the hole in the crystal. Three thin strips of mica, each about 2 cm. long and 2 mm. wide, are inserted in the space left between the electrode rod and the crystal, so that the ends of these mica pieces project perhaps 1 cm. below the cup. The mica strips are cut so wide that they have to be pushed into place. They serve to hold the rod in the crystal and keep the lower gold washer in place. The cup can now be grasped by its edge with a pair of tweezers and the electrode rod pushed through the hole in the bottom of the bomb. It is then bolted down. It is next tested to make sure that there is no short circuit between the electrode and the bomb; and finally, to make sure that the joint is tight, the bomb is connected once more to the pump.

If, after the bomb has been in use for some time, it is necessary to remove the lower electrode, it may be done in the following way: The nut *N* can not be unscrewed, but enough of it can be removed with saw and file so that the remainder will slip through the hole in the brass washer. A light direct blow with the hammer on the end of the electrode rod is then always sufficient to start it out. The brass remaining in the threads of the electrode rod is easily removed with any pointed tool, and the electrode is ready to use again.

The cover *B* is made slightly concave to allow the air bubbles, which might otherwise collect under it, to escape into the electrode chamber above. To line the cover a round disk of platinum-iridium alloy containing 15 per cent iridium is taken, and the two tubes, T_1 and T_2, are soldered to this with pure gold. This alloy is used rather than pure platinum on account of its greater hardness, which prevents the gold ring from cutting into it.

In the development of the bomb, the tube T_2 has probably caused more trouble than any other part. This is due in part to the fact that at high temperatures the pressure is sufficient to force water through the lining at any unsupported spot. If the tube was made of heavy metal, and especially when it was made of the 2 per cent alloy, it was itself capable, owing to its small diameter, of withstanding the pressure without expanding enough to come into perfect contact with the steel at all points; as a result, the bomb would leak at such points. Or, owing to the greater difficulty in mechanically expanding the small tube to meet the shell, the fit would be so poor at the start that the hydraulic pressure would tear it. Our earlier work here was done with the 2 per cent alloy before we fully realized the great difference in ductility between this and pure platinum. Because of its extreme ductility gold was then tried. This worked beautifully at first, but finally failed because the 22-carat gold solder employed in making the tube disintegrated under the action of the hot water. Recourse was then had to pure platinum, which completely solved the difficulty. The platinum tube is first expanded by driving in some plugs of cotton with the help of a hammer and a brass rod almost as large as the inside of the tube. Seamless tubing might be advantageously used here, but we used a tube made of sheet platinum soldered with pure gold, and this proved to be entirely satisfactory.

The small tube T_1 is conveniently made by rolling up tightly some thin sheet platinum and then flowing gold in to fill the spaces between the convolutions. This gold is fed in from the outside, while the whole tube is kept hot in a large blast-lamp flame. Care must be taken not to use too much gold; otherwise a drop may form inside the tube, and its removal by drilling is extremely difficult. Owing to capillary forces, no gold will go to the space inside until the smaller spaces between the convolutions are all filled, so that there is no danger so long as too much gold is not employed. In this, as in all other operations when gold is used in soldering platinum, the piece should be kept hot no longer than is absolutely necessary, because the gold rapidly alloys with the platinum, and the resulting alloy is more crystalline in structure than either of the constituents and has not their ductility. To make the joint between T_1 and the lining of the cover stronger, the tube is reinforced above this point, as shown by the drawing. This was necessary in our earlier apparatus before the lining was screwed down to the cover, but is probably not necessary in the later form.

As the upper end of the tube T_1 is to act as a valve-seat, and as therefore there will be a good deal of downward pressure at this point, the tube has to be well expanded into the conical cavity in the steel at *V* (fig. 1). Because of this, and of the further fact that the valve-seat should be as soft as possible, it is better to make the upper end of T_1 of solid gold, boring it out later. This is done as follows: The tube is first packed full of asbestos, to prevent gold from getting into it. A band of thin platinum foil is next wound tightly around the upper end and bound on by means of a platinum wire. This band is then pushed partly off of the end of the tube, so as to make a small projecting tube; and pure gold is melted into this until it is full. The platinum foil on the outside of the gold is now filed off. Both tubes are now attached to the cover lining and inserted in place in the cover. Holding the lower end of T_1 on an anvil, the soft gold, projecting perhaps 3 mm. above the steel at *V*, is compressed with a riveting hammer. The asbestos is now drawn out of the tube, and a hole is drilled down through the gold to meet the hole in the platinum.

The valve-seat at the start is of the form shown in fig. 1, and the slightest pressure on the steel bicycle ball serves to force the ball down into the soft gold tube enough to make the joint tight. But after this process has been repeated a few times the bearing surface of the ball on the gold becomes so large that the pressure which can be obtained by tightening the screw *K* with the fingers is not sufficient to make the joint tight. The valve-seat can be easily brought back to its original condition, however, by filling the depression, which the ball has made, with soft dental gold and opening the hole again with a scratch awl or a drill. The filling is most conveniently accomplished with a little "moss fiber" gold, using the regular dental tool. Of course the top should always be left concave, so that the ball will of itself roll to the center. Time is saved in the end by putting the valve-seat in order each time; for, if this is done, there will never be a leak at this point. It is also better to use a fresh steel ball each time. The screw *K* should fit well, but still turn easily with the fingers; for, if there were much friction here, it would be impossible to tell how much of the force employed in screwing it down was being communicated to the ball and how much was wasted in friction in the screw. Smearing a little vaseline on the screw prevents air from leaking in while the bomb is being evacuated.

The edge of the lining is fastened to the cover by eight steel screws, in the same way as the flange of the lining of the body of the bomb is secured, the only difference being that it is not necessary at the top to recess the edge of the platinum. Care must, of course, be taken that the screws in the top do not come opposite those in the lower part when the top is put on. Two reference marks enable the experimenter to bring the cover always into the same position with respect to the bottom.

The cover lining is forced into place and tested, just as was the lining of the lower part of the bomb, by means of the Cailletet pump, making the pump connection with a metal piece like that shown in fig. 6, which takes the place of the lower part of the bomb.

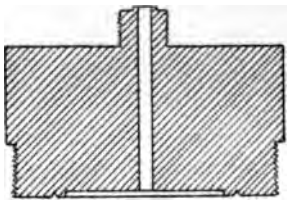

Fig 6.

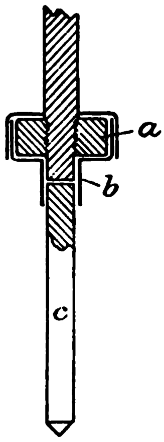

Fig 7.

The construction of the auxiliary electrode is similar to that of the lower one; it will be evident from fig. 7. The part *a* has to be made just as small as is consistent with making the joint tight on the end of the crystal. The platinum covering consists of a little platinum box similar to that used on the lower electrode, a short piece of tubing *b* and a piece of platinum wire *c*.

The gold packing-rings are made as follows: A piece of gold wire about 3 mm. shorter than the circumference of the finished ring is cut off and the ends fused together in a small oxy-gas flame. (The ends of the wire were originally filed flat and then soldered with coin gold; but this method besides being much more laborious had the disadvantage of bringing base metal into the gold.) The joint made in this way is slightly thicker than the rest of the ring, but not enough so to do any harm. The ring is then annealed and placed on a cast-iron spreader. By pushing a tapered brass plug into this spreader, it is expanded and the ring stretched. By placing a reference mark on the tapered plug, the ring can be stretched to just the same size every time. It, of course, comes off perfectly round, and after reannealing is ready for use. Each ring is used but once; but after a number have been used they are melted down and made into fresh wire.

The total weight of platinum used in our bomb is about 185 grams. This, together with the fine construction work involved, makes the initial cost considerable, but the platinum, of course, retains the larger part of its value. We have estimated that the cost of reproducing such a bomb, including the labor of a machinist and all the materials except the platinum, is about 125.

Before adopting the sheet-platinum lining, attempts were made to produce a satisfactory platinum plate on the inner surface of the bomb by the electrolytic process described by Langbein;* but although a firmly adhering deposit was obtained, it was found not to be dense enough to protect the surface beneath from attack and the liquid from consequent contamination.

6. PROCEDURE FOR THE CONDUCTIVITY MEASUREMENTS.

In making a set of conductivity determinations, the valve-seat at the top of the tube, T_1 (fig. 1), is first put in order by putting in a gold filling, as has already been described in section 5. Then any loose particles of graphite or dirt adhering to the flange and cover in the neighborhood of the gold packing-ring are removed with absorbent cotton saturated with benzene, and the screw thread on the lower part is cleaned in the same manner. Both the upper and lower parts are now rinsed thoroughly with good water, using the fine stream from a wash bottle to remove more effectually any loose particles of graphite which may have got into the bomb upon previously opening it. By this means, too, water can be forced through the fine tube, T_1. If the solution to be investigated is a dilute one, the rinsing must be very thorough. Finally the bomb is rinsed out with some of the solution, and as much as possible of this is then shaken out. The bomb is then ready for use.

Suppose now it is desired to make a series of measurements at the temperatures up to 281°. An amount of solution which will almost, but not quite, fill the bomb at this temperature is measured in from a pipette previously graduated to contain this amount, as will be described in section 7. A gold packing-ring is annealed and cleaned by heating it in the flame of a burner, and it is placed in the groove. The cover is then put in place, taking care not to disturb the ring. The thread in the large nut is next washed out with benzene, to get rid of any solid substance which may have condensed there in a previous heating. With a piece of cloth or absorbent cotton, a lot of finely powdered graphite is then rubbed into the thread and upon the surface which bears on the brass compensating washer. The nut is now screwed on by hand, care being taken not to disturb the cover; otherwise it might be raised slightly, so that particles of graphite would enter the bomb. The apparatus is next transported carefully to the large wrench, and the nut is tightened up. The air pressure is then reduced to about 2 cm. by connecting the small tube with a Richards water pump, the valve is screwed down, the lead-wires bolted on, and the bomb is ready for the measurements.

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*Langbein's Electro-Deposition of Metals, 378 (1902).

The conductivity is first measured at 26°. To hasten the equalization of the temperatures, the cold bomb was usually introduced after bringing the bath to about 30°. The other vapor baths are heated up meanwhile.

The bomb is then immersed in the 140° bath, whereupon the conductivity increases very rapidly. The minimum in the telephone is at first greatly disturbed by the boiling of the solution, which takes place strongly at the lower electrode, owing to the fact that this is at the start, because of its position, the hottest part of the bomb. But as the temperature of the solution approaches that of the bath the disturbance decreases, and finally ceases altogether. When the temperature has become almost constant, which is indicated by the constancy of the conductivity, the bomb is removed from the bath, shaken, and returned as quickly as possible. To shake it while hot, a piece of asbestos cloth, with a piece of woolen cloth outside, is used. If the shaking is omitted, the measured conductivity may be too high by as much as 0.5 per cent. This was found to be due to the following facts: At 140° there is still a considerable vapor space left in the bomb, the entire cover being above the liquid surface. During the first part of the heating the xylene vapor is condensed so rapidly by the bomb that it extends up only for a little distance above the bottom of the bomb, leaving the upper part completely out of it. This causes an evaporation of pure water and a condensation of it all over the colder cover, leaving the solution too concentrated. If the bomb is shaken after reaching the temperature of the bath and quickly returned, the same action does not repeat itself, since the top is now as hot as the bottom. The bridge readings are now continued (usually for about 30 minutes) till one perfectly constant for 10 to 15 minutes is obtained.

The bomb is then transferred to the naphthalene bath. Shaking was found to have no effect at this temperature, owing, doubtless, to the fact that the liquid level has then risen almost to the cover, so that large drops can not adhere to the latter, and to the fact that the surface tension has diminished, so that less water is held clinging to the walls of the narrow chamber in the cover.

The bomb is next brought into the 281° bath. It is now necessary to keep constant watch of the conductivity between the upper auxiliary electrode and the walls of the bomb, so as to be sure that too much solution has not been put into the bomb. The reasons for putting in solution enough at the start to so nearly fill the bomb at the highest temperature are first, to reduce the vapor space at all the temperatures as much as possible, since a correction has to be made for the amount of solvent in this space; and secondly, to see that the bomb is absolutely tight even at the highest temperature, when the solution is in contact with the upper electrode. This latter is important, since a leak, if it took place above the liquid level, would cause a loss of pure solvent and a consequent increase in the concentration of the solution.

After completing the measurements at 281°, the bomb is returned to the 218° bath, then to the 140° bath, and finally it is brought back to 26°. In going from a higher temperature to a lower much time is saved by cooling the bomb, in front of a fan outside the bath, to a temperature which is at least as low as that next desired; for while heating in a vapor bath is rapid, the cooling in it of a hotter body is very slow. During the first half of the experiment, where the bomb is introduced each time into a hotter bath, stirring inside the bomb takes place of itself, it being accomplished by the rising vapor bubbles and the rapid convection currents caused by the bottom of the bomb being so much hotter than the top during the heating. During the second half it is necessary to provide for this by shaking the bomb before putting it into each bath. How much shaking is necessary can be determined by repeating the operation and seeing whether the conductivity has been affected by it.

The advantages derived from cooling the bomb down through the same series of temperatures and again taking measurements are that these furnish a check on the accuracy of the preceding ones, and especially that they show whether or not there has been any contamination, and if so, between what temperatures it took place and to how much it amounts.

The bomb is opened as soon as the experiment is completed, since otherwise there may be trouble in getting the cover off because of the strong adhesion of the gold packing-ring to the platinum lining below. This effect increases with use, since a small amount of gold from the ring adheres to the platinum each time, and subsequent rings will adhere more firmly to this gold than they would to a clean platinum surface. The effect can easily be reduced, however, as soon as it grows troublesome, by rubbing the platinum cover, where it comes in contact with the ring, with a burnisher and by marking in the groove with a lead pencil. The trace of graphite which adheres to the surface is very effective.

When the bomb is not in use, good water is left standing in the lower part. The cover is inverted and the upper chamber similarly kept filled with water. If for the next experiment a more dilute solution is to be employed, the bomb must first be heated with good water to perhaps 218° for some little time. No amount of rinsing or soaking out at ordinary temperatures will answer the purpose. There is on this account a great saving of time effected by beginning with the most dilute solution to be investigated, and afterwards measuring those more and more concentrated.

Our measurements at 306° were carried out, for the most part, after complete experiments up to 281° had been made, so that they usually consisted merely of measurements at 26°, 306°, and again at 26°.

7. PROCEDURE FOR THE SPECIFIC-VOLUME MEASUREMENTS.

To determine the specific volume of a solution at any temperature, such an amount of solution is weighed into the bomb as will bring the liquid level up onto the auxiliary electrode at that temperature. This amount was determined by successive heatings with increasing volumes of solution.

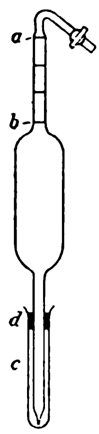

Fig 8.

A pipette of the form represented by fig. 8 was made for each of the temperatures 218°, 281°, and 306°. The stem is graduated between *a* and *b*, and the capacity up to these points is roughly determined by weighing. The volume of the pipette is made such that for water or dilute solutions it will deliver the right amount into the bomb when filled up to the point *b*. For more concentrated solutions the expansion is less, so that more of the solution must be used. The graduations on the pipette serve only as an indication of how much solution to take. The exact amount used is obtained by weighing the pipette filled and then again after discharging. During the weighing the tip is covered with a small test tube *c*, which is held on by the rubber band *d*.

The bomb is first dried out by rinsing it with alcohol and ether. The residue left by these solvents upon evaporation is sufficient to affect the conductivity of the diluter solutions employed, so that no attempt was made to determine the conductivity of such solutions at the same time as their specific volume. The solution is boiled to expel the air. This increases the concentration slightly; but this is of no consequence if, as was usually the case, the experiment was made solely to determine the specific volume. If it was also to serve for conductivity measurements, the solution was boiled gently in a tall platinum vessel which was weighed with its contents before and after boiling. This gave the loss of solvent during the operation. Knowing this and the amount of solution originally present in the cylinder, the final concentration is easily calculated. After weighing the solution in from the pipette, the bomb is closed, and the air pressure reduced to 2 cm. Upon heating, careful watch is kept of the readings with the auxiliary electrode to make sure that too much solution has not been put in. After the conductivity of the upper chamber has been constant long enough to show conclusively that the temperature has become stationary and that the bomb is absolutely tight (even the slightest leak being of course indicated by a constant decrease in the conductivity of the upper chamber), the conductivities between the walls of the bomb and both the upper and lower electrodes are measured carefully, and the temperature of the bath is observed. The experiment is then complete.

The ratio of these two conductivities is calculated, and the corresponding volume is obtained by interpolation from a plot obtained as described in section 8. This volume, corrected for the expansion of the bomb and then divided by the weight of solution in the bomb, gives the specific volume of that solution at the temperature in question, and this quantity divided by the specific volume of the solution at 4° gives the volume of that quantity of the solution that would at 4° occupy one cubic centimeter, this quantity being most convenient in subsequent computations.

8. STANDARDIZATION OF THE APPARATUS.

THERMOMETERS.

These were calibrated by the method recommended by Crafts,* first for irregularities of bore and then at the fixed points 0°, 100°, 218°, and 306°. For the last two temperatures the vapors of boiling naphthalene and of benzophenone were used. These substances were obtained from Kahlbaum, and were purified in the manner suggested by Crafts, until their melting-points came within his limits. The form and dimensions of the vapor bath used in establishing the 218° and 306° points were essentially those given by him. To reduce the temperatures lying between the fixed points to the gas scale, Crafts' corrections for French glass were also used, our thermometers being of the same make as those used by him. The values adopted for the boiling-points of the naphthalene and benzophenone on the hydrogen-gas scale were, however, those recently obtained by Jaquerod and Wassmer (J. chim. phys., **2**, 72; 1904). At the beginning every temperature measurement was followed by a lag ice-reading; but this was found to be unnecessary, since the thermometers showed no lag. The ice-reading was, however, taken frequently, to make sure that the zero did not change from another cause — evaporation of mercury

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*Am. Chem. J., **5**, 307-338 (1883-84).

from the bulb below and condensation in the chamber above. This effect was not apparent even after long use at temperatures up to 280°; but above this the zero would fall perhaps 0.1° from two or three days' use. When in use at 306°, instead of taking an ice-reading the thermometer was first placed in the benzophenone heater and then in the calibrating apparatus containing perfectly pure benzophenone. The difference in reading (usually amounting to 0.1° to 0.2°) was deducted from the true boiling-point of benzophenone at the observed barometric pressure.

Two thermometers were calibrated in this way, and in actual use their corrected readings were always found to agree satisfactorily with each other.

SLIDE-WIRE BRIDGE AND RESISTANCE COILS.

The slide wire was calibrated by the method of Strouhal and Barus.* The resistance coils were calibrated by comparison with a standard bridge of the Massachusetts Institute of Technology.

THE CONDUCTANCE-CAPACITY.

In order to reduce the observed to specific conductances, the conductance-capacity or so-called "cell-constant"† was determined in the usual manner, by measuring in the bomb solutions of known conductance. For this purpose the measurements at 26° of the solutions of both potassium and sodium chlorides, which were afterward studied at higher temperatures, were employed, the mean of the most reliable of them being taken. These data are given in section 13.

THE VOLUME OF THE SOLUTION IN THE BOMB AND THE CORRESPONDING CONDUCTANCE-RATIO.

It was stated above that the volume of the solution at any time in the bomb was determined by measuring the ratio of the conductances between the walls of the bomb and the lower and upper electrodes respectively. This ratio will hereafter be called the conductance-ratio. Its value is, of course, independent of the nature of the solution in the bomb, and is determined fully by its height in the narrow chamber, and therefore by its volume. To find the values corresponding to different volumes, we proceed as follows: The bomb is first dried by rinsing it with alcohol and ether.

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*Wied. Ann., **10**, 326 (1880). See also Kohlrausch and Holborn, Leitvermögen der Elektrolyte, 45 (1898).

†The term cell-constant is inappropriate, since the value varies with the temperature. We shall adopt the expression conductance-capacity, which seems fairly descriptive, since the quantity may be defined as the specific conductance of a solution which, when placed in the vessel, gives rise to an actual conductance unity.

Some 0.02 normal potassium chloride solution* is then boiled to free it from air, and, right after cooling, enough of this to fill the bottom part of the bomb to within 1 or 2 mm. of the flange is weighed in from a pipette. The mouth of the pipette is kept under the surface to diminish the absorption of air. The cover is next put on and screwed down, care being taken not to tip the bomb enough to get any of the solution into the mouth of the capillary tube. By means of the water pump the air pressure in the bomb is reduced to about 2 cm., and the valve is then closed. If the air is not removed from the solution at the start, it comes out rapidly upon reducing the pressure and spatters some of the solution up into the tube, thus allowing it to be swept out by the air current.

The lead wires are now bolted on and the bomb is placed in the liquid xylene bath, serving ordinarily for the 26° measurements, and the temperature of the latter is raised by means of the heating coil. The liquid level in the bomb is at the start about 3 mm. below the point of the auxiliary electrode, so that the resistance of the upper cell is shown by the conductivity apparatus to be infinite; but upon heating, the level rises and finally touches the electrode, whereupon the resistance suddenly sinks to perhaps 1,000 ohms. The temperature of the bath (perhaps about 130°) is now held constant until the solution in the bomb has also attained it, as will be indicated by the resistance of the lower and, far more sensitively, by that of the upper cell becoming constant. Both these resistances are then noted, and the temperature is measured.

The temperature is now raised by steps of three or four degrees until that ratio of the conductances is reached which corresponds to the bomb being almost completely full. This limiting ratio can be determined cold at any time by measuring the resistance of the lower cell and then inverting the bomb and measuring that of the upper cell. Finally, the conductance-ratios are plotted as abscissas and the corresponding volumes as ordinates, whereby a straight line is obtained.

The computation of the volumes is made with the help of the following data: Zepernick and Tammann† have found that equal volumes of a 0.52 normal potassium chloride solution and of water at 0° upon heating from that temperature to 140° become different from each other by only 0.1 per cent. It is therefore perfectly safe to assume that the expansion of the 0.02 normal potassium chloride solution used by us is the same as that of pure water. From Hirn's‡ results the specific volume of water at the temperature in question, but under a pressure of 14.8 atmospheres, may be obtained. At 135°, the mean temperature of the calibration experiments, the vapor pressure is 3.1 atmospheres. Hirn's result should then be reduced to this pressure. The coefficient of compressibility of water has been investigated by Pagliani and Vicentini* up to 100°. By plotting their values and extrapolating, 0.000048 is found for the coefficient at 135°, or for the fractional decrease in volume per atmosphere pressure. Hirn's value should then be increased by $0.000048 \times (14.8 - 3.1) \times 100 = 0.056$ per cent. Multiplying the value so obtained by the weight of solution employed and by the specific gravity of the cold solution referred to water at the same temperature, the volume corresponding to the observed conductance-ratio is obtained.

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*The reasons for taking this solution instead of pure water are that it makes the conductance at the upper electrode high enough to give a good minimum, and that the solution is so strong that contamination can not possibly make any trouble.

†Z. phys. Chem., **16**, 665 (1895).

‡G. A. Hirn, Ann. chim. phys., (4), **10**, 32 (1897). His series of observations covers the range of temperature up to 180°. Between 110° and 143° his values differ from those found by Zepernick and Tammann by only 0.02 per cent.

9. PREPARATION OF THE SUBSTANCES AND SOLUTIONS.

The sodium chloride used was purified by precipitation with hydrochloric acid gas. It was then washed with hydrochloric acid, dried, and finally ignited until decrepitation ceased.

The potassium chloride was precipitated twice with hydrochloric acid gas, crystallized from hot water, dried, and finally ignited.

Solutions were made up, by weighing out the salts, so as to be almost exactly 0.1 and 0.01 normal at 4°. The solutions of smaller concentration were made by diluting the 0.01 normal one with the help of two graduated flasks.

The equivalent weights used are as follows: K = 39.14, Na = 23.05, Cl = 35.46. All weighings were reduced to a vacuum.

The water used throughout this investigation was prepared by redistilling ordinary distilled water to which alkaline permanganate solution was added from a steam-jacketed copper still with a tin condenser. The first quarter of the distillate was rejected, and the following portions were condensed hot (between 60° and 90°). The water had a specific conductance of $(0.7 \text{ to } 1.0) \times 10^{-6}$ reciprocal ohms.

10. DISCUSSION OF THE SYSTEMATIC ERRORS AND THEIR CORRECTION.

ERRORS AFFECTING THE SPECIFIC-VOLUME VALUES.

(1) In calculating the specific-volume, the volume of the bomb was directly determined at about 135°, as described in section 8, and the expansion of the metal from this point to the temperatures of the experiments was corrected for Andrews,† working with "soft" cast steel, which corresponds to the material from which the bomb was constructed, found

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*Landolt-Börnstein-Meyerhoffer, Tabellen, 60 (1905).

†Proc. Roy. Soc., **43**, 299 (1887).

the mean coefficient of cubical expansion between 100° and 300° to be 0.0000450; and this value was adopted for the corrections. The difference between his steel and that used in the bomb can hardly be great enough to cause an appreciable difference in the coefficient of expansion, since his values for two steels as different as Bessemer steel with 0.15 per cent combined carbon, and cast steel with 0.45 per cent, differ by only 6 per cent; and an error of even 6 per cent in the coefficient of expansion would produce a maximum error, even at 306°, of only 0.05 per cent in the specific volume.

(2) The quartz-crystal cup expands upon heating, thus diminishing the volume of the bomb occupied by the solution. The correction for this, even at 306°, amounts to only —0.03 per cent.

(3) The bomb expands owing to the pressure within. At 306°, where this correction is greatest, the vapor pressure plus the air pressure may be estimated at 100 atmospheres. Assuming that the modulus of elasticity of the steel is 17,372 kgm. per sq. mm., which is the value found by Pisato* at 300°, the volume correction due to this cause is + 0.025 per cent. This is opposite in sign and essentially equal to the preceding correction; they therefore eliminate each other.

(4) The volume of the tube T_1 is only 0.07 c.cm. or 0.06 per cent of the whole volume of the bomb. It is therefore so small that no irregularities in the extent to which it is filled with solution could much affect the result.

(5) The volume of the bomb depends somewhat on the extent to which the large nut is tightened up and the gold packing-ring compressed. Four of the gold rings which had been used were chosen at random, and the mean thickness of each was calculated from measurements made at eight equidistant points with a micrometer caliper. The average deviation from the mean thickness of these rings was such as to affect the volume of the bomb by only 0.02 per cent. So this source of error can be unhesitatingly disregarded, especially as each final specific-volume value is the mean of the values obtained from several independent experiments.

(6) The bomb is never completely filled with liquid, the vapor space amounting, on an average, to about 1 c.cm. or 0.8 per cent of the total volume of the bomb (about 124 c.cm.). A certain fraction of the water is therefore vaporized, and the specific volume appears too small by a corresponding amount. The specific volume of the vapor is not yet known above 200°. By extrapolation, however, from the values up to 200°, the specific volume of the vapor at 218° is found to be seventy-five times that of the liquid. From this it follows that at 218° the correction is only $\frac{1}{124} + \frac{1}{75}$, or about 0.01 per cent. Such a calculation is not possible at the higher temperatures, 281° and 306°; but that no considerable error

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*Nuovo Cimento (3), 4, 152 (1878).

arises from this source was shown by direct experiments. For example, when two or more specific-volume determinations were made, the amount of solution taken in the different experiments was purposely varied, so that the vapor space should vary from about 1.8 c.cm. to 1 c.cm. If, now, a considerable amount of the water were present in the vapor space, the specific-volume values obtained would, of course, be larger the smaller that space. As a matter of fact, however, the values obtained with the 1 c.cm. vapor space were as often smaller as they were larger than those obtained with the 1.8 c.cm. vapor space. In other words, no difference greater than the variable experimental error was observed. The error due to this source is therefore probably less than 0.1 per cent.

(7) The temperature measurements may be regarded as accurate to within 0.2°; and this of itself introduces an uncertainty of only 0.07 per cent in the worst case, that of the 306° values. That the bomb and its contents actually attained the temperature of the surrounding vapor is shown by the fact that the extremely sensitive reading of the upper electrode remained constant indefinitely after it had once become so; and by the fact that there could not be a continuous loss of heat of appreciable magnitude from the bomb to the surroundings, since upon the sides the bomb was protected against radiation and cold convection-currents by the iron shield with the vapor outside, and since above there was always a layer of vapor 10 cm. in height, and since the dropping back of condensed liquid onto the bomb was prevented by the mica shield; moreover, the copper lead-wires were only 1.2 mm. in diameter and passed through the upper layer of vapor before emerging.

(8) Another possible source of error might be the gathering of vapor bubbles on the under surface of the cover, whereby the apparent volume of the liquid would be increased. That this did not occur was shown by removing the bomb from the heater, shaking vigorously, immediately replacing it, and taking conductivity readings as soon as the temperature had again become constant, whereby the same readings were obtained as before the shaking.

(9) The air was not entirely removed from the bomb at the start, and, as the solution expands, and the temperature rises, the air pressure increases. Assuming that the preliminary boiling had removed all of the air from the solution in the beginning, and that there is no solubility of the air in the liquid at the high temperatures, its pressure can be calculated by the gas laws. At the temperatures of 218°, 281°, and 306°, it would thus amount to about 1, 2, and 2.5 atmospheres respectively. The effect of these air pressures on the specific-volume values can not be calculated, since the compressibility at these temperatures is not known; but for these small pressures it is undoubtedly less than the errors of observation.

(10) If the vapor above the solution had an appreciable conductance it would make the conductance between the upper electrode and the bomb appear too great. But this is not the case, as is shown by the fact that unless the liquid is in contact with the electrode there is no measurable conductance here, even at 306° with a 0.1 normal potassium chloride solution. We can at present assign only an upper limit to the conductance of the vapor; but it certainly does not exceed $\frac{1}{200000}$ part of that of the solution.

ERRORS AFFECTING THE CONDUCTANCE VALUES.

(1) All the errors in the values of the specific volume have an effect of the same magnitude upon those of the equivalent conductance, with the important exception of that due to the amount of solvent in the vapor space at the two highest temperatures, 281° and 306°. No error arises from this last source for the reason that, owing to the increase in concentration of the solution, the specific conductance increases in the same proportion as the volume diminishes; for at 281° and 306° (but not at 140° and 218°) the quantity of liquid in the bomb was the same in the two series of measurements.

(2) The conductance-capacity might be expected to vary with the height of the liquid level in the bomb, but direct experiment showed that for the range of the liquid level in our measurements the effect of this was less than the error of observation. The smallest amount of solution employed in any of the experiments was first introduced into the bomb and the conductance measured at 26°. Then more of the same solution was introduced until the liquid was in contact with the whole cover; but the resistance was not measurably changed. Mr. A. C. Melcher has shown (see section 36, Part IV) that even much larger variations in the quantity of solution have no effect.

(3) The conductance-capacity changes with the temperature owing to two causes: first, the expansion of the quartz-crystal cup; and, secondly, that of the bomb itself. A direct experimental investigation of the effect on the conductance of such changes in the dimensions of the cup and bomb has been made by Mr. A. C. Melcher and is described in section 36, Part IV. The corrections for the conductance-capacity have been based on his results. The relative values at the different temperatures are given in section 13.

(4) The effect of the pressure on the conductance-capacity is entirely negligible. For at 306° the radius is increased by the pressure 0.01 per cent, and this affects the conductance-capacity by even less.

(5) The resistance of the lead-wires has to be deducted from the measured resistance of the bomb; and, since a portion of the leads is subjected

to the temperature of the bath, this correction is different for different temperatures. This resistance may be considered as made up of three parts: R_1, the constant resistance of the heavy leads; R_2, the resistance of the small leading-in wires, L_1 and L_2; and R_3, that of the steel electrode rod. R_1 and R_2 were measured at room temperature. For the other temperatures R_2 was calculated from its value at room temperature. R_3 was calculated from its dimensions and the specific resistance of steel. The maximum value (at 306°) of the total resistance of the lead-wires was 0.061 ohms.

(6) In the case of the more dilute solutions it was necessary to correct for the conductance of the water used. To do this, some water prepared in the same way and of the same conductance cold as that used for making up the solutions was put into the bomb, and just such a set of experiments was made with it as had been made with the solutions. Then for any temperature the conductance of the water, measured at that same temperature and under the same conditions, was deducted from that of the solution. This at the same time corrects for contamination, since, with a dilute, neutral-salt solution, there is no apparent reason why the contamination should not be the same as for water. For the most dilute solution used, 0.0005 normal, the maximum correction (at 306°) amounts to 1.9 per cent. See also section 14.

(7) In the conductivity experiments, the vapor space at 140° and 218° was considerable, so that at these temperatures a correction has to be applied for the vaporized solvent, since the solution is more concentrated than it would otherwise be. This correction was calculated from the known volume of the vapor in the bomb and its specific volume, using for the latter the data of Zeuner* which go up to 200°, and extrapolating for the 218° value. The correction amounts to + 0.05 per cent at 140° and + 0.18 per cent at 218°. As explained above, it is not required in the case of the 281° and 306° values.

(8) The temperature measurement at 26° is certainly more accurate than the work requires. Above this, the temperature reading is probably correct to 0.2°. Most of the uncertainty in the equivalent conductance values introduced by this possible error finds expression in the specific-volume values, and this has already been considered. Besides this there is the much smaller effect on the observed resistance of the bomb. The total uncertainty in the equivalent conductance arises from both these sources; that due to 0.2° is in the worst case (at 218°) 0.09 per cent, and where, as has usually been the case, several experiments are made and the mean taken, this effect tends to be eliminated.

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*Landolt-Börnstein-Meyerhoffer, Tabellen, 62 (1905).

11. THE SPECIFIC-VOLUME DATA.

All of the measurements have been included in table 1 (page 36) with the exception of two, which, though agreeing well with the others, were known to be less reliable.

The first and second columns are self-explanatory.

The third column gives the concentration of the solution at 4°, expressed in milli-equivalents per liter.

The fourth column gives the corrected temperature of the measurement.

The fifth column gives the number of grams of solution which were weighed into the dry bomb at the start.

The sixth column gives the volume, expressed in cubic centimeters, which, at the temperature (135°) at which the bomb was calibrated, corresponds to the observed conductance-ratio. This volume was obtained by interpolation from a plot made as described in section 8. The actual volume occupied by the solution at the higher temperature is greater than this by an amount equal to the expansion of the bomb upon heating from 135° to that temperature. The temperature-coefficient of volume expansion of the steel shell of the bomb is assumed to be 0.000038 per degree.

The seventh column gives the specific volume of the solution at the temperature of observation. It is obtained by dividing the values of the preceding column, after correcting them for the expansion of the bomb as just described, by the weight of solution given in the fifth column.

The last column gives the ratio of the specific volume at the round temperatures 218°, 281°, and 306°, to that of the same solution at 4°. Thus, this ratio shows the volume occupied by that quantity of solution which at 4° has a volume of 1 c.cm. The values are obtained from those of the preceding column by reducing them to these temperatures by means of the temperature-coefficient obtained from our specific-volume values, and then dividing the results by the specific volumes of the solutions at 4°. These specific volumes are as follows: 0.9958 for 0.1 normal, and 0.9996 for 0.01 normal sodium chloride; and 0.9954 for 0.1 normal, and 0.9995 for 0.01 normal potassium chloride.*

12. SUMMARY OF THE SPECIFIC-VOLUME VALUES.

The final results are brought together in table 2 (page 36). The value at 140° is that found by Hirn† for pure water reduced from the higher pressure which he employed to the vapor-pressure.

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*These values were computed from the densities given by Kohlrausch and Hallwachs (Wied. Ann., **50**, 122, 1893) for NaCl at 18°, and from that given by Kohlrausch (Leitvermögen der Elektrolyte, 76) for a normal KCl solution at 18°, under the assumptions that the change in density is proportional to the concentration and that the expansion is the same between 4° and 18° for these solutions as for water.

†Hirn, Ann. chim phys. (4), **10**, 32 (1867).

TABLE 1.—*The specific-volume data.*

Date.	Substance.	Milli-equivalents per liter.	Temperature.	Weight of solution.	Volume uncorrected.	Specific volume.	Specific volume ratio.
1902							218°/4°.
Mar. 31 .	NaCl	2	216.4	104.16	122.75	1.1831	1.1858
Apr. 2 ..	"	"	216.8	104.58	123.58	1.1863	1.1885
Apr. 3 ..	"	"	217.5	103.44	122.18	1.1859	1.1868
	Mean..	....	....	....	....	....	1.1870
May 2 ..	NaCl	100	217.6	103.52	121.79	1.1862	1.1869
							281°/4°.
Apr. 14 ..	NaCl	2	280.5	92.11	122.08	1.3343	1.3358
Apr. 14 ..	"	"	280.6	92.97	123.51	1.3374	1.3387
Apr. 18 ..	"	"	280.6	92.65	122.94	1.3359	1.3371
	Mean..	....	....	....	....	....	1.3372
Apr. 29 ..	NaCl	100	280.7	92.83	122.07	1.3237	1.3302
May 1 ..	"	"	280.2	93.27	122.37	1.3207	1.3290
June 19 .	"	"	281.3	93.34	122.85	1.3248	1.3287
	Mean..	....	....	....	....	....	1.3293
1903							306°/4°.
Mar. 11 .	NaCl	2	305.7	85.40	121.82	1.4373	1.4385
Mar. 27 .	"	"	305.2	85.35	121.30	1.4318	1.4352
	Mean..	....	....	....	....	....	1.4368
Feb. 20 ..	NaCl	10	306.1	85.69	122.14	1.4362	1.4362
Jan. 17 ..	NaCl	100	304.6	86.39	120.94	1.4106	1.4226
Mar. 31 .	"	"	304.6	87.01	121.92	1.4117	1.4237
	Mean..	....	....	....	....	....	1.4232
Feb. 17 ..	KCl	10	304.1	85.61	121.24	1.4270	1.4360
Feb. 18 ..	"	"	305.4	85.76	122.01	1.4335	1.4367
	Mean..	....	....	....	....	....	1.4363
Jan. 30 ..	KCl	100	304.3	86.75	121.56	1.4119	1.4258
Feb. 10 ..	"	"	305.7	86.78	122.05	1.4171	1.4248
Feb. 16 ..	"	"	304.7	86.41	121.29	1.4143	1.4264
*Feb. 16 .	"	"	304.7	86.41	121.24	1.4137	1.4258
	Mean..	....	....	....	....	....	1.4257

*Same solution as in preceding experiment, after cooling, shaking, and reheating.

TABLE 2.—*Ratio of the specific volume at various temperatures to that at 4°.*

Substance.	Equivalent concentration at 4°.	Specific-volume ratio.				
		26°.	140°.	218°.	281°.	306°.
NaCl	0.002	1.0032	1.0803	1.1870	1.3372	1.4368
"	0.01	"	"	......	......	1.4362
"	0.1	"	"	1.1869	1.3293	1.4232
KCl	0.01	"	"	......	......	1.4363
"	0.1	"	"	......	......	1.4257

The results with the 0.002 normal solution may be regarded as completely identical with those that would be obtained with pure water; for this solution contains only about 0.01 per cent of salt; and, moreover, the experiments themselves show that there is no difference between the specific-volume ratio of the 0.002 and 0.01 normal solutions, and that the difference between the latter and that of the 0.1 normal solution is somewhat less than 1 per cent, which indicates that the order of magnitude of the difference between pure water and the 0.002 normal solution is 0.02 per cent. The specific volume of water is therefore 1.187 at 218°, 1.337 at 281°, and 1.437 at 306°. It is, according to our estimate of the possible errors, almost certain that these values are not in error by as much as 0.3 per cent, and it is probable that the error does not exceed half this amount. Previous determinations of the specific volume of water at high temperatures have been made by Hirn up to 180°, by Waterston* up to 320°, and by Ramsay and Young† up to 270°. The values obtained by interpolation from the older results of Waterston are 1.194 at 218°, 1.355 at 281°, and 1.454 at 306°, which are seen to be considerably higher than ours. Ramsay and Young, however, found 1.188 at 218° in substantial agreement with our value.

Attention may also be called to the facts that the 0.1 normal solutions between 218° and 306° expand appreciably less than pure water, but that the difference between the solutions of the two salts scarcely exceeds the experimental error.

13. THE CONDUCTANCE-CAPACITY OF THE APPARATUS.

The conductance-capacity was calculated from the conductance measurements at 26°, using for the specific conductances of the 0.1 and 0.01 normal potassium chloride solutions the standard values of Kohlrausch, Holborn, and Diesselhorst,‡ and for the other solutions the values at 18° of Kohlrausch and Maltby,‖ and the temperature-coefficients of Déguisne.§ The quartz-crystal cup which was used for the first half of the measurements (cell I) was accidentally broken, and a new one had to be substituted for the rest of the work. After making three experiments with the new cup, the platinum lining of the lower part of the bomb had to be removed and repaired, and this operation changed the conductance-capacity. The term cell II_a will be used to characterize the bomb as it was in these first three experiments with the new cup, and the

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*Phil. Mag. (4) **26**, 124 (1863).

†Phil. Trans. (A), **183**, 109 (1892).

‡Wied. Ann., **64**, 440 and 451 (1898).

‖Wissensch. Abhandlungen phys.-techn. Reichsanstalt, **3**, 210 (1900).

§Dissertation, Strassburg (1895); Kohlrausch and Holborn, Leitvermögen der Elektrolyte, **199**.

term cell II as it was in all subsequent work. With these exceptions, the conductance-capacity calculated from measurements made at widely different periods did not vary throughout the work. Even when the electrode was removed because of a leak, and then replaced, it did not make any measurable difference, as was, indeed, to be expected, since the value is so largely determined by the dimensions of the quartz cup. The values of the conductance-capacity, with the solutions from which they were derived, are given in table 3. The unit of conductance employed here and throughout this publication is the reciprocal ohm.

TABLE 3.—*Conductance-capacity at 26°.*

Cell I.			Cell II.		
Substance.	Milli-equivalents per liter.	Conductance-capacity.	Substance.	Milli-equivalents per liter.	Conductance-capacity.
KCl	100	0.8294	KCl	100	0.9853
NaCl	100	0.8288	"	10	0.9845
"	10	0.8280	"	2	0.9850
KCl	2	0.8280	NaCl	2	0.9840
NaCl	2	0.8317	Mean of first two values		0.9849
Mean of first three values		0.8287	Cell II_a.		
			NaCl	100	0.9949

The original data from which these were calculated are all given in tables 5 and 6. Each value is the mean of all of the values calculated from all of the experiments on the solution in question at 26°.

The values derived from the 0.002 normal solutions are not included in the means, because, owing to the higher dilution, they are probably not so reliable as the others. They are given here, especially to show that our conductance measurements were not affected either by polarization or by unsymmetry in the telephone; for had this been the case, our capacity values calculated from these solutions would not have agreed with those derived from the 0.1 normal solutions.

As explained in section 10, the conductance-capacity changes with the temperature; the percentage corrections to be applied at the different temperatures of the experiments to the values of it at 26° are as follows: — 0.23 at 140°; — 0.41 at 218°; — 0.56 at 281°; and — 0.58 at 306°.

14. THE WATER CORRECTION.

The conductance of the water at the various temperatures of the experiments was subtracted from the measured conductance of the solution. Two experiments, the data of which are given in table 4, served as a basis for the correction. For a fuller discussion of this correction see section 10.

The last two lines give the percentage corrections to be applied at the various temperatures to the observed conductances in the case of a 0.002 normal sodium chloride solution. They are given so as to show the order of magnitude of these corrections. The correction decreases of course in the same proportion as the specific conductance of the solution increases.

TABLE 4.—*Observed conductance* ($\times 10^6$) *of water in the bomb.*

Date.	Cell No.	26°.		140°.		218°.		281°.	306°.
		Initial.	Final.	Initial.	Final.	Initial.	Final.		
May 14, 1902.	I	0.85	1.25	3.57	4.55	6.1	6.5	7.3	....
Feb. 28, 1903.	II	1.02	1.67	....	....	....	....	....	7.1
Percentage correction	I	0.28	0.41	0.33	0.42	0.41	0.43	0.45	....
	II	0.38	0.62	....	....	....	....	....	0.53

15. THE CONDUCTIVITY DATA.

Table 5 (pp. 40, 41) contains the conductivity data for the various solutions. The first four columns require no explanation further than the statement that the concentration is expressed in milli-equivalents per liter as has been done throughout this series of articles unless otherwise noted. The fifth column gives the concentration at the temperature of the measurement, corrected in the case of the 140° and 218° values for the solvent in the vapor space. The correction is made as explained in section 10, and amounts to + 0.05 per cent at 140° and + 0.18 per cent at 218°. The sixth column contains the observed resistances of the bomb, expressed in ohms, after correcting for errors in the resistance coils and slide wire, and deducting the resistance of the lead-wires. The seventh column gives the equivalent conductance obtained by dividing the conductance-capacity for the given temperature by the concentration at *t*° (given in the fifth column) and by the resistance (given in the sixth column) after correcting it for the water, and by multiplying the result by 10^6.

TABLE 5.—*Conductivity data for sodium chloride.*

Date.	Cell No.	Concentration at 4°.	Temperature, $t°$.	Concentration at $t°$.	Resistance.	Equivalent conductance.
1902 June 23	I	0.4995	25.91	0.4979	12945	127.18
			140.6	0.4624	3564	496.1
			218.6	0.4212	2565	753.6
			281.1	0.3733	2333	932.9
			218.8	0.4210	2571	751.9
			141.9	0.4617	3538	498.8
			25.91	0.4979	12835	127.67
June 25	I	0.4995	25.91	0.4979	12932	127.31
			141.2	0.4621	3554	497.8
			218.9	0.4213	2573	751.1
			281.1	0.3733	2333	933.4
			219.1	0.4213	2566	752.6
			142.2	0.4616	3494	505.1
			25.91	0.4979	12614	129.84
June 26	I	0.4995	25.91	0.4979	12921	127.42
			280.8	0.3736	2333	932.7
			219.2	0.4208	2565	754.0
			139.2	0.4630	3586	490.8
			25.91	0.4979	12782	128.15
1903 Mar. 18	II	0.4992	26.00	0.4987	15305	127.05
			306.2	0.3472	2732	1012.4
			26.00	0.4987	15163	127.02
1902 May 8	I	2.018	25.91	2.012	3293.0	124.76
			280.9	1.509	604.0	899.9
			25.91	2.012	3277	125.18
May 9	I	1.998	25.91	1.991	3326	124.76
			280.9	1.494	608.3	902.8
			25.91	1.991	3314	125.05
			138.8	1.852	927	497.4
			217.3	1.685	669.6	728.4
			25.91	1.991	3313	125.09
May 10	I	1.998	25.91	1.991	3322	124.91
			139.9	1.850	923.8	482.2
			217.9	1.686	669.3	728.4
			281.0	1.495	608.9	901.6
			217.9	1.686	669.0	728.7
			140.1	1.850	921.0	483.3
			25.91	1.991	3310.8	125.18
1903 Mar. 3	II	1.995	26.00	1.989	3926	125.65
			306.6	1.386	720.5	975.6
			26.00	1.989	3909	125.87
1902 May 15	I	9.990	25.92	9.967	687.62	120.92
			138.8	9.274	194.35	458.7
			218.5	8.438	141.54	690.9
May 16	I	9.990	25.91	9.967	688.10	120.83
			139.0	9.271	194.09	459.6
			218.0	8.440	141.30	692.0

TABLE 5.—*Conductivity data for sodium chloride*—Continued.

Date.	Cell No.	Concentration at 4°.	Temperature, t°.	Concentration at t°.	Resistance.	Equivalent conductance.
1902 May 20	I	9.990	25.91	9.967	687.99	120.85
			139.3	9.267	193.20	461.8
			218.0	8.440	141.70	690.0
			283.1	7.441	131.62	841.4
			218.0	8.440	141.86	690.0
			139.9	9.261	193.59	461.2
			25.91	9.967	688.28	120.80
1903 Feb. 20	II	9.977	306.1	6.944	156.37	901.9
			26.00	9.945	803.6	123.24
Feb. 21	II	9.977	305.8	6.950	156.50	900.3
1902 Apr. 29	I	102.75	25.91	102.42	74.55	108.54
			280.7	77.33	15.823	673.5
			139.6	95.20	21.568	402.7
			217.4	86.80	16.278	584.1
			25.91	102.42	74.52	108.59
Apr. 30	I	103.11	25.91	102.78	74.25	108.60
			138.5	95.65	21.550	401.2
			217.4	87.13	16.217	584.1
May 1	I	101.53	25.91	101.18	75.12	109.03
			280.2	76.49	15.905	677.4
			218.4	85.63	16.418	587.1
			139.1	94.15	21.810	402.7
			25.91	101.18	75.12	109.03
May 2	I	101.48	25.91	101.14	75.35	108.75
			217.5	85.56	16.524	583.8
			139.8	93.95	21.787	404.0
June 18	I	99.90	25.91	99.57	76.44	108.88
			140.2	92.48	22.018	406.1
June 19	I	99.90	25.91	99.57	76.28	109.10
			140.3	92.48	21.926	407.8
			281.3	75.09	16.226	676.7
			218.2	84.28	16.701	586.4
			141.2	92.41	21.965	407.4
			25.91	99.57	76.23	109.19
1903 Jan. 15	II_a	99.90	25.94	99.58	91.90	108.71
			305.1	70.39	20.35	690.7
			25.94	99.58	91.72	108.93
Jan. 17	II_a	99.90	25.94	99.58	91.72	108.93
		99.90	304.6	70.51	20.30	691.3
			25.94	99.58	91.72	108.93

TABLE 6.—*Conductivity data for potassium chloride.*

Date.	Cell No.	Concentration at 4°.	Temperature, *t*°.	Concentration at *t*°.	Resistance.	Equivalent conductance.
1903 Mar. 20	II	0.4999	26.00	0.4983	12981	150.32
			305.5	0.3484	2611	1056.5
			26.00	0.4983	12763	151.70
1902 Aug. 20	I	2.001	25.91	1.994	2790.4	148.56
			140.2	1.853	828.0	537.4
			218.0	1.689	618.9	786.8
			281.5	1.494	574.0	957.1
			218.1	1.689	619.3	786.2
			140.3	1.853	824.7	539.4
			25.91	1.994	2778.5	149.04
Aug. 25	I	2.001	25.91	1.994	2785.6	148.82
			140.0	1.853	824.8	539.4
			218.6	1.687	616.1	791.1
			281.0	1.496	573.6	956.4
			218.9	1.686	617.2	790.0
			140.4	1.852	820.8	542.1
			25.91	1.994	2726.8	151.87
1903 Mar. 2	II	1.997	26.00	1.991	3308.6	149.02
			306.0	1.390	685.8	1028.2
			26.00	1.991	3298.0	149.18
Feb. 17	II	10.04	304.1	7.006	148.58	940.9
Feb. 18	II	10.04	305.4	6.977	148.94	942.4
			25.96	9.972	675.0	146.31
Feb. 19	II	10.04	25.96	9.972	681.8	144.87
Mar. 28	II	10.04	26.00	9.972	685.1	144.18
1902 Aug. 28	I	100.14	25.91	99.72	63.17	131.56
			141.2	92.56	19.760	452.1
			220.8	84.04	15.360	639.4
			281.9	74.22	15.223	729.3
			220.8	84.04	15.341	640.2
			141.2	92.56	19.701	453.5
Aug. 29	I	100.14	25.91	99.72	63.30	131.29
			141.6	92.52	19.724	453.1
Sept 2	I	100.14	25.91	99.72	63.30	131.15
			141.2	92.54	19.783	451.7
			217.8	84.45	15.406	634.3
			141.8	92.48	19.735	453.1
Sept. 27	I	100.14	25.91	99.72	63.04	131.83
			280.7	74.43	15.160	730.3
1903 Jan. 30	II_a	99.92	304.3	70.46	19.094	728.0
Feb. 10	II	99.92	305.7	70.15	19.068	732.3
			25.94	99.60	75.30	131.34
Feb. 13	II	99.92	25.94	99.60	75.30	131.34
Feb. 16	II	99.92	304.7	70.36	19.043	731.8

16. SUMMARY OF THE EQUIVALENT CONDUCTANCE VALUES REDUCED TO ROUND TEMPERATURES AND CONCENTRATIONS.

The separate conductance values given in tables 5 and 6 were all corrected so as to correspond to the uniform temperatures of 26°, 140°, 218°, 281°, and 306° by means of temperature-coefficients obtained by plotting those values. The so-corrected equivalent conductances are summarized in the following table. The concentration in table 7 is expressed in milli-

TABLE 7.—*Equivalent conductance at round temperatures.*

SODIUM CHLORIDE.

Date.	Concentration at 4°.	26°.		140°.		218°.		281°.	306°.
		Initial.	Final.	Initial.	Final.	Initial.	Final.		
1902									
June 23..	0.4995	127.48	127.97	494.2	492.6	751.5	749.1	933.0	......
June 25..	0.4995	127.61	130.14	493.9	497.9	748.0	748.8	933.0	......
June 26..	0.4995	127.72	128.45	.....	493.5	.....	749.9	933.2	......
1903									
Mar. 18..	0.4992	127.05	127.02	.....	.....	.....	.....	.....	1011.5
Mean..	......	127.46	*128.85 127.02	494.0	494.7	749.7	748.3	933.1	1011.5
1902									
May 8..	2.018	125.05	125.47	.....	.....	.....	.....	900.1	......
May 9..	1.998	125.05	125.38	.....	483.3	.....	730.5	903.0	......
May 10..	1.998	125.20	125.47	482.6	483.1	728.7	729.0	901.5	......
1903									
Mar. 3..	1.1995	125.65	125.87	.....	.....	.....	.....	.....	973.9
Mean..	......	125.24	*125.44 125.87	482.6	483.2	728.7	729.8	902.2	973.9
1902									
May 15..	9.990	121.16	......	462.4	.....	689.7	.....	.....	......
May 16..	9.990	121.10	....	462.6	.....	692.1	.....	.....	......
May 20..	9.990	121.12	121.07	464.0	461.6	690.1	690.1	836.6	......
1903									
Feb. 20..	9.977	......	......	.....	.....	.....	.....	.....	901.4
Feb. 21..	9.977	......	......	.....	.....	.....	.....	.....	900.5
Mean..	......	121.11		462.6		690.5		836.6	901.0
1902									
Apr. 29..	102.75	108.77	108.82	.....	403.8	.....	585.2	673.7	......
Apr. 30..	103.11	108.83	......	405.1	.....	585.2	.....	.....	......
May 1..	101.53	109.26	109.26	.....	405.0	.....	586.2	678.1	......
May 2..	101.48	108.98	......	.....	404.5	584.7	.....	.....	......
June 18..	99.90	109.11	......	405.7	.....	.....	.....	.....	......
June 19..	99.90	109.33	109.42	407.1	404.4	.....	585.8	676.1	......
1903									
Jan. 15..	99.90	108.87	109.09	.....	.....	.....	.....	.....	691.0
Jan. 17..	99.90	109.09	......	.....	.....	.....	.....	.....	......
Jan. 17..	99.90	......	109.09	.....	.....	.....	.....	.....	691.6
Mean..	......	109.07		405.1		585.4		676.0	691.3

*These two means refer to the experiments carried to 281° and to 306°, respectively.

TABLE 7.—*Equivalent conductance at round temperatures*—Continued.

POTASSIUM CHLORIDE.

Date.	Concentration at 4°.	26°.		140°.		218°.		281°.	306°.
		Initial.	Final.	Initial.	Final.	Initial.	Final.		
1903									
Mar. 20..	0.4999	150.32	151.70	.....	.....	.....	.....	.....	1057.6
Mean .	......	150.32	151.70	.....	.....	.....	.....	.....	1057.6
1902-03									
Aug. 20..	2.001	148.87	149.35	536.7	538.4	786.9	786.0	955.8	......
Aug. 25..	2.001	149.13	152.18	539.4	540.7	789.4	787.4	966.4	......
Mar. 2..	1.997	149.02	149.18	.....	.....	.....	.....	.....	1022.0
Mean..	......	149.01	*150.77 149.18	538.0	539.6	788.2	786.7	956.1	1022.0
1903									
Feb. 17..	10.04	......	......	.....	.....	.....	.....	.....	941.9
Feb. 18..	10.04	......	146.42	.....	.....	.....	.....	.....	943.5
Feb. 19..	10.04	144.87	......	.....	.....	.....	.....	.....	......
Mar. 28..	10.04	144.18	......	.....	.....	.....	.....	.....	......
Mean..	......	145.16		.....	.....	.....	.....	.....	942.7
1902									
Aug. 28..	100.14	131.81	......	448.9	450.3	633.6	634.4	729.4	......
Aug. 29..	100.14	131.54	......	448.9	.....	.....	.....	.....	......
Sept. 2..	100.14	131.40	......	448.0	448.4	634.7	.....	.....	......
Sept. 27..	100.14	132.08	......	.....	.....	.....	.....	730.4	......
1903									
Jan. 30..	99.92	......	......	.....	.....	.....	.....	.....	726.5
Feb. 10..	99.92	131.51	......	.....	.....	.....	.....	.....	732.3
Feb. 13..	99.92	131.51	......	.....	.....	.....	.....	.....	......
Feb. 16..	99.92	......	......	.....	.....	.....	.....	.....	730.7
Mean..	......	131.64		448.9		634.2		729.9	729.8

*These two means refer to the experiments carried to 281° and to 306°, respectively.

equivalents per liter at 4°. In the columns headed "Initial" are given the equivalent conductances obtained from the measurement at the temperature in question before going to the higher temperatures; while in the columns headed "Final" are given the equivalent conductances obtained after returning to the temperature in question from the higher ones. From a comparison of the separate initial values at any temperature and concentration the degree of agreement of the determinations made at different times, and often with different solutions, will be seen. A comparison of the initial and final values in the separate experiments shows the contamination that resulted from the heating. In the cases of the 10 and 100 milli-normal solutions where the contamination is insignificant, both the initial and final values have been included in deriving the mean; in the other cases, the means of the initial values and of the final values have been taken separately.

Table 8 contains a summary of best values derived from the means in table 7. The general mean of the initial and final values has been directly transferred in the cases of the 100 milli-normal and (except at 306°) of the 10 milli-normal solutions. In the other cases we have adopted the mean of the initial values after correcting it for contamination when this amounted to more than 0.25 per cent, as shown by the differences between the initial and final values at 26°. This contamination-correction is based on the experience that when a solution has once been heated to the highest temperature of any experiment it undergoes no further change of importance either upon continued heating at that temperature or upon cooling and reheating. Therefore the difference in initial and final values at 26° corresponds to the change that had already taken place in the solution when the measurement at the highest temperature was made. Since, however, the conductance of the contaminating substance, if it be a base or acid, would have a smaller temperature-coefficient than that of the salt, it seemed best to apply a percentage correction equal to only two-thirds of this difference at 26°.* Instead of reproducing our 26° values in table 8, we have inserted the more accurate ones of Kohlrausch and Maltby at 18°.†

TABLE 8.—*Best values of equivalent conductance at round temperatures.*

Temperature, t°.	Sodium chloride.		Potassium chloride.	
	Concentration at t°.	Equivalent conductance.	Concentration at t°.	Equivalent conductance.
18	0.5	107.18	0.5	128.11
	2.0	105.55	2.0	126.31
	10.0	101.95	10.0	122.43
	100.0	92.02	100.0	112.03
140	0.463	491.5	1.85	535.0
	1.85	482.0	93.0	449.0
	9.26	462.5	....	....
	95.2	405.0	....	....
218	0.420	745	1.68	782
	1.68	727	84.4	634
	8.43	690	....	....
	86.6	585	....	....
281	0.373	925	1.49	949
	1.48	900	74.3	730
	7.47	836	....	....
	77.6	676	....	....
306	0.346	1011	0.347	1051
	1.38	973	1.38	1022
	6.93	895	6.96	937
	70.2	691	70.2	730

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*Mathematically expressed the fractional correction in general at any temperature t is $\frac{2}{3}\left(\frac{\Lambda_{26}\,(\text{Init} - \Lambda_{26}(\text{Fin})}{\Lambda_{26}} - \frac{\Lambda_{t}\,(\text{Init}) - \Lambda_{t}\,(\text{Fin})}{\Lambda_{t}}\right)$, the last term dropping out at the highest temperature of each series of experiments.

†Wissensch. Abhandl. phys.-techn. Reichsanstalt, **3**, 210 (1900).

In order to compare the conductivity values at different temperatures, it is desirable to correct those directly measured for the change in concentration produced by the expansion when a given solution is heated. The values in table 8, which, owing to this expansion, refer at different temperatures to somewhat different concentrations, as is there indicated, have been reduced to the nearest round concentrations, by a graphic interpolation with the help of the nearly linear function $\frac{1}{\Lambda}=\frac{1}{\Lambda_0}+K(C\Lambda)^{0.5}$ (See section 17.) The so-reduced values are presented in table 9.

In the subsequent stages of these researches various other measurements of the conductivity of sodium and potassium chloride solutions have been made by other experimenters, namely, by A. C. Melcher, by G. W. Eastman, and by H. C. Cooper. This has been done partly as a control and partly in order to complete this first series of measurements. The details and original data of these experiments will be presented in the later articles of this series;* but in order to simplify and shorten the discussion of the results we have included all of their final values, together with our own, in table 9. Our values are indicated by adding the letters N–C to the data, those of A. C. Melcher by the letter M, of G. W. Eastman by the letter E, and of H. C. Cooper by the letters Cp. The best final values which we have derived by combining all these data, a double weight being usually assigned to the later determinations, are printed in black type in the table. The values at 18° are those of Kohlrausch and Maltby. The values at 0° for potassium chloride are means derived from the closely concordant determinations of Whetham† and of Kahlenberg.‡ All the other data in the first table for potassium chloride were obtained by G. W. Eastman in this laboratory. The values given in parentheses for zero concentration were obtained by graphic extrapolation with the help of the empirical formula $\frac{1}{\Lambda_0}=\frac{1}{\Lambda}-K(C\Lambda)^m$, as described in section 17.

In this table, as in all those containing final values throughout this publication, the concentration is expressed in milli-equivalents per liter, using as atomic weights the values given by the International Commission for 1905; the temperature is expressed on the hydrogen-gas scale, using for the reduction to this scale at 218°, 281°, and 306° the values found for the boiling-points of naphthalene and benzophenone by Jaquerod and Wassmer; and the equivalent conductance is expressed in reciprocal ohms and refers to a concentration at the temperature under which it stands equal to the value given opposite to it in the first column.

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*See section 41, Part IV, and section 54, Part V.
†Z. phys. Chem., **33**, 351 (1900).
‡J. Phys. Chem., **5**, 348 (1901).

TABLE 9.—*Final values of the equivalent conductance.*

SODIUM CHLORIDE.

Concentration.	18°.	100°.	140°.	156°.	218°.	281°.	306°.
0.0	**109.0**	**362**	**500**	**555**	**760**	**970**	**1080**
0.5	....	....	491 N-C.	....	743 N-C.	922 N-C.	1003 N-C.
"	....	355.5 Cp.	....	545 Cp.	738 Cp.	....	....
0.5	**107.2**	**355.5**	**491**	**545**	**740**	**922**	**1003**
2.0	....	....	481 N-C:	....	723 N-C.	895 N-C:	959 N-C.
"	....	349.0 E.	....	....	....	....	954 M.
"	....	349.0 Cp.	....	534 Cp.	722 Cp.	....	....
2.0	**105.6**	**349.0**	**481**	**534**	**722**	**895**	**955**
10.0	....	....	461 N-C:	....	685 N-C.	821 N-C.	870 N-C.
"	....	....	....	....	685 M.	820 M.	857 M.
"	....	335.5 Cp.	....	511 Cp.	684 Cp.	....	....
10.0	**102.0**	**335.5**	**461**	**511**	**685**	**820**	**860**
80.0	....	....	411 N-C.	....	590 N-C.	674 N-C.	676 N-C.
"	....	301.0 E.	....	450.5 E.	591 M.	674 M.	682 M.
80.0	**93.5**	**301.0**	**411**	**450.5**	**500**	**674**	**680**
100.0	....	....	403.5N-C.	....	....	....	....
"	....	296.0 E.	....	441.5 E.	....	....	....
100.0	**92.0**	**296.0**	**403.5**	**441.5**	....	....	....

POTASSIUM CHLORIDE.

Concentration.	0°	18°.	25°.	50°.	75°.	100°.	126°.
0.0	**81.4**	**130.1**	(152.1)	(232.5)	(321.5)	**414**	**(519)**
0.5	**80.5**	**128.1**	....	....	....	....	....
2.0	**79.6**	**126.3**	146.4	....	....	**393.0**	....
10.0	**77.5**	**122.4**	141.5	215.2	295.2	**377.0**	470.0
80.0	**72.8**	**113.5**	....	....	....	**341.5**	....
100.0	**71.5**	**112.0**	129.0	194.5	264.6	**336.0**	415.0

Concentration.	140°.	156°.	218°.	281°.	306°.
0.0	**565**	**625**	**825**	**1005**	**1120**
0.5	....	....	....	....	**1044** N-C.
2.0	**534** N-C.	**588** E.	**779** N-C.	**980** N-C.	**1008** N-C.
10.0	....	560 E.	741 M.	874 M.	909 M.
"	....	....	....	....	912 N-C.
10.0	....	**560**	**741**	**874**	**910**
80.0	455 N-C.	....	637 N-C.	**724** N-C.	716 N-C.
"	....	489 E.	640 M.	722 M.	722 M.
80.0	**455**	**498**	**638**	**723**	**720**
100.0	**446.5** N-C.	**489.5** E.	....	....	....

An examination of table 9 shows that the results obtained independently by the various experimenters in this laboratory with different sets of apparatus and different solutions agree in almost all cases within 0.2 to 0.3 per cent, except at the temperature of 306°, but that at this temperature there are several deviations of nearly 1 per cent. Except at this highest temperature the agreement is entirely satisfactory and indicates a corresponding precision of the results; and even at 306° it is probable that the final values adopted are not in error by more than 0.3 per cent, since the later measurements made in larger number and after more experience by Mr. A. C. Melcher are probably more accurate than our own.

17. CHANGE OF EQUIVALENT CONDUCTANCE WITH THE CONCENTRATION.

It is a well-known fact that the mass-action law does not express even approximately the change with the concentration of the ionization of salts and strong acids and bases, when this, in accordance with the familiar hypothesis of the ionic theory, is calculated from the conductance ratio Λ/Λ_0. This has led to the proposal of numerous other functions,* which have for their purpose an accurate representation of the experimental values of the equivalent conductance and the ionization values deduced therefrom. The extended discussion of the matter has not yet led to any conclusion, so far as the theoretical explanation of the phenomenon is concerned. There have, however, been discovered some simple empirical formulas which at ordinary temperatures express the observed results satisfactorily.

Those which contain only a single arbitrary constant† have the following form when expressed in terms of the equivalent conductance (Λ) at any concentration C and the limiting conductance Λ_0 at zero concentration:

$$\frac{\Lambda_0 - \Lambda}{C^{\frac{1}{2}}} = K \text{ (Kohlrausch)} \qquad \frac{\Lambda_0 - \Lambda}{\Lambda^{\frac{1}{2}}\, C^{\frac{1}{2}}} = K \text{ (Barmwater)}$$

$$\frac{\Lambda_0 - \Lambda}{\Lambda^{\frac{3}{2}}\, C^{\frac{1}{2}}} = K \text{ (van't Hoff)} \qquad \frac{\Lambda_0 - \Lambda}{\Lambda^{2}\, C^{\frac{1}{2}}} = K \text{ (Rudolphi)}$$

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*Compare Kohlrausch, Wied. Ann., **26**, 200 (1885); **50**, 394 (1893); MacGregory, ibid., **51**, 133 (1894); Barmwater, Z. phys. Chem., **28**, 134, 428 (1899); Sabat, ibid., **41**, 224 (1902); Muller, Compt. rend., **128**, 505 (1899); Rudolphi, Z. phys. Chem., **17**, 385 (1895); van't Hoff, ibid., **18**, 300 (1895); Kohlrausch, ibid., **18**, 662 (1895); Storch, ibid., **19**, 13 (1896); Bancroft, ibid., **31**, 188 (1899); Jahn, ibid., **37**, 499 (1901); **41**, 265, 288 (1902); Nernst, ibid., **38**, 493 (1901); Bousfield, ibid., **53**, 263 (1905); Kohlrausch and Maltby, Wissensch. Abhandl. phys.-techn. Reichsanstalt, **3**, 219 (1900); Kohlrausch, Sitzungsber., preus. Akad., **44**, 1002 (1900); Kohlrausch and Steinwehr, ibid., 1902, 581; Kohlrausch and Grüneisen, ibid., 1904, 1215.

†Kohlrausch and Maltby (loc. cit., p. 219) and Kohlrausch and Grüneisen (loc. cit.) find that the formula $\Lambda_0 - \Lambda = KC^{\frac{1}{2}}$ applies closely to the results with uni-univalent, uni-bivalent, and bi-bivalent salts between 0.002 and 0.0001 normal, but that large deviations exist at higher concentrations, even at 0.01 normal.

It seemed therefore to be of especial interest to test the applicability of these formulas at the widely different temperatures employed in our experiments. When such a test is made by direct substitution the results are in a high degree dependent on the values of Λ_0 employed, since in dilute solutions $\Lambda_0 - \Lambda$ is a relatively small quantity; yet in several instances authors have not given sufficient consideration to this matter. The most satisfactory method of procedure seems to us to be the elimination of the Λ_0 value, which can not be determined with sufficient accuracy by extrapolation, by writing the functions in the following form:

$\Lambda = \Lambda_0 - K\,C^{\frac{1}{3}}$ (Kohlrausch) $\Lambda = \Lambda_0 - K\,\Lambda^{\frac{1}{3}}\,C^{\frac{1}{3}}$ (Barmwater)
$\Lambda = \Lambda_0 - K\,\Lambda^{\frac{3}{2}}C^{\frac{1}{2}}$ (van't Hoff) $\Lambda = \Lambda_0 - K\,\Lambda^2\,C^{\frac{1}{2}}$ (Rudolphi)

and then plotting the values of Λ along one coordinate axis and those of the C-Λ function constituting the last term (that is, $C^{\frac{1}{3}}$, $\Lambda^{\frac{1}{3}}\,C^{\frac{1}{3}}$, etc.) along the other axis. If the function in question holds, the points will of course lie upon a straight line; and by comparing, in the case of the different functions, the deviations of the separate points from the best representative straight line that can be drawn, a measure of the degree of applicability of each function is obtained. All our complete series of measurements and those of Kohlrausch and Maltby on the same salts at 18° have been studied in this way, a plot on a very large scale being employed. The straight lines were drawn in every case so as to represent most closely the points for the concentrations 100 or 80, 10, and 2 millinormal, and the average of the percentage deviations of the observed Λ values at these three points taken. These averages for the two functions are given in the following table under $C^{\frac{1}{3}}$ and $(C\Lambda)^{\frac{1}{3}}$, respectively.

TABLE 10.—*Mean percentage deviations of the observed values of the equivalent conductance from those calculated by the cube-root functions.*

Temperature.	Sodium chloride.		Potassium chloride.	
	$C^{\frac{1}{3}}$	$(C\Lambda)^{\frac{1}{3}}$	$C^{\frac{1}{3}}$	$(C\Lambda)^{\frac{1}{3}}$
18	0.1	0.15	0.05	0.05
100	0.05	0.1	0.1	0.05
140	0.05	0.1	....	....
156	0.1	0.15	0.15	0.05
218	0.15	0.2	0.2	0.3
281	0.45	0.35	0.05	0.1
306	0.4	0.4	0.45	0.3

It will be seen that the deviations from either function are insignificant up to 156°, but that they become considerable at the higher temperatures. It may be of interest to state also the percentage deviations of our straight line corresponding to the Kohlrausch function from the points representing the conductances of sodium and potassium chloride at 18° in the still more dilute solutions investigated by Kohlrausch and Maltby. These deviations are — 0.53 and — 0.42 per cent, respectively, in case of the 0.0001 normal solutions, and — 0.36 and — 0.25 per cent, respectively, in that of the 0.0002 normal solutions. Thus this function does not satisfactorily represent the results at very low concentrations, and seems therefore unsuitable for obtaining the value (Λ_0) at zero concentration. Moreover, this function, as well as that of Barmwater, does not seem to admit of any theoretical interpretations, since it does not even correspond to any functional relation between the concentrations of the ions and un-ionized molecules.

The fact that the van't Hoff equation does not satisfactorily express the results with many salts* at 18° and 25° has led to the suggestion by Storch and later by Bancroft that a general expression of the form $\Lambda_0 - \Lambda = K\Lambda^n C^{n-1}$ be employed, the exponent n being varied as required by the results with different salts. An equation of this general form has the advantage that it does express the concentrations of the ions and un-ionized substance as a function of each other. This becomes obvious when the function is written in the form $C(\Lambda_0 - \Lambda) = K(\Lambda C)^n$, which is equivalent to $C(1-\gamma) = \text{const.} \times (C\gamma)^n$, where γ is the conductance ratio (Λ/Λ_0) or the fraction of the salt ionized. That such an expression with three arbitrary constants (assuming that Λ_0 is to be determined with the help of the function itself) can be made to express the conductivity fairly accurately through a considerable range of concentration is obvious. It is nevertheless of interest to determine what values of the exponent n must be used for different salts and for the same salts at different temperatures. For this purpose it is best to write the equation in the form

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + K_1(C\Lambda)^{n-1}$$

and to plot the values of $\frac{1}{\Lambda}$ against those of $(C\Lambda)^{n-1}$, the exponent being given successively different values (in the neighborhood of 0.5) until the points fall as nearly as possible on a straight line. We have done this with the final values for sodium and potassium chloride given in table 9.

The values of the exponent n so found at various temperatures are given in table 11. It was usually possible to determine them within 0.02. It will be seen that the exponent varies but little with the temperature, and that the results do not correspond at all closely at any temperature with the mass-action law, which requires the exponent 2.

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*See Kohlrausch and Maltby, loc. cit., p. 222.

TABLE 11.—*Values of the exponent n in the function* $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$.

Substance.	0°.	18°.	100°.	140°.	156°.	218°.	281°.	306°.
KCl	1.50	1.42	1.40	....	1.40	1.48	1.50	1.48
NaCl	....	1.42	1.48	1.48	1.50	1.50	1.47	1.46

This form of function seems to us to furnish the best means of determining the value of Λ_0, at any rate in cases where a series of accurate measurements at very small concentrations is not available; we have therefore employed this method generally throughout this series of investigations. The values of Λ_0 given in table 9 (except those at 18° which were derived by Kohlrausch and Maltby) were obtained in this way by graphic extrapolation upon the plots just referred to.

It is interesting to compare the Λ_0 values to which this method leads with those derived by Kohlrausch and his co-workers at 18° by application of the function $\Lambda_0 - \Lambda = KC^{\frac{1}{2}}$ to his own conductivity-values at very small concentrations (0.1 to 2 milli-normal). We have made the necessary calculations for seven salts of two different types with the following results. The table also contains the results obtained by Kohlrausch by applying the function $\Lambda_0 - \Lambda = KC^{\frac{1}{2}}\Lambda^p$ at concentrations between 0.1 and 100 milli-normal.

	KCl.	NaCl.	KNO₃.	AgNO₃.	Ba(NO₃)₂	K₂SO₄.	CaCl₂.
Λ_0 by $\Lambda_0 - \Lambda = K(C\Lambda)^{n}$*.	130.6	109.8	126.3	115.7	117.0	134.7	119.0
Λ_0 by $\Lambda_0 - \Lambda = KC^{\frac{1}{2}}\Lambda^p$...	130.1	109.0	126.5	115.8	117.7	133.5	117.5
Λ_0 by $\Lambda_0 - \Lambda = KC^{\frac{1}{2}}$.....	129.9	108.9	126.4	115.8	117.0	132.5	116.7

The values of Λ_0 obtained from the conductances at moderate concentrations either by the Storch function or the Kohlrausch function $\Lambda_0 - \Lambda = KC^{\frac{1}{2}}\Lambda^p$ are seen to be usually somewhat higher than those derived from the conductances at very low concentrations; but the differences are not as a rule very important, being less than 1 per cent, except in the last two cases.

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*Assuming $n - 1 = 0.42$ for KCl and NaCl, 0.50 for KNO_3, 0.52 for $AgNO_3$, 0.55 for $Ba(NO_3)_2$, 0.45 for K_2SO_4, and 0.40 for $CaCl_2$, which are the values which give a most nearly linear function between 2 and 50 milli-normal. With K_2SO_4, however, no value of the exponent gave a fully satisfactory expression of the conductance values. Incidentally it is of interest to note that the conductance value at 100 milli-normal was greater than that required by the assumed function by the following percentage amounts: 0.36 for KCl, 0.00 for NaCl, 0.06 for $AgNO_3$, 0.00 for $Ba(NO_3)_2$, 0.4 for K_2SO_4, and 0.3 for $CaCl_2$.

18. CHANGE OF THE EQUIVALENT CONDUCTANCE WITH THE TEMPERATURE.

We shall in this section confine our considerations almost wholly to the effect of temperature on the conductance (Λ_0) extrapolated for zero concentration; for at higher concentrations the equivalent conductance of the salt is the product of two factors — the degree of ionization of the salt and the equivalent conductance of its ions; and the first of these factors is best discussed separately, as will be done in section 19.

Attention may first be called to the fact that the limiting conductances of the two salts approach equality as the temperature increases; thus the ratio of $\Lambda_{0(NaCl)}$ to $\Lambda_{0(KCl)}$ has the following values at the various temperatures:

18°	100°	140°	156°	218°	281°	306°
0.84	0.87	0.88	0.89	0.92	0.96	0.96

The percentage difference in the migration-velocities of the potassium ion and sodium ion, therefore, becomes less, the higher the temperature.

In order to show more clearly the character of the relation between migration-velocity and temperature we have calculated the mean temperature-coefficients ($\Delta\Lambda_0/\Delta t$) for the successive temperature-intervals, and these were found to be as follows:

	0–18	18–50	18–100	50–100	100–156	156–218	218–281	281–306
KCl	2.70	3.20	3.46	3.63	3.77	3.23	2.86	4.60
NaCl	....	....	3.09	....	3.44	3.31	3.33	4.40

It will be seen that up to about 156° the temperature-coefficient of the conductance values extrapolated for zero concentration increases steadily, and then, between 156° and 281°, decreases markedly in the case of potassium chloride and remains nearly constant in the case of sodium chloride, while above 281° a pronounced increase again takes place with both salts.

It is also of interest to compare the fractional change in equivalent conductance with that in the viscosity of the water; for the former is doubtless more closely related to the latter than to any other simple physical property. The viscosity (η) of water has been measured by several experimenters at temperatures below 100° and by de Haas at 124°, 142°, and 153°.[*] In the table on the next page are given in the same columns the ratio $(\Lambda_0)_{t_2}:(\Lambda_0)_{t_1}$ for potassium chloride and $\eta_{t_1}:\eta_{t_2}$ for water for a number of consecutive pairs of temperature. The values of the viscosity η

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[*] See Landölt-Börnstein-Meyerhoffer, Physigalisch-chemische Tabellen, p. 76. de Haas' values are 0.00223 at 124°, 0.00193 at 142°, and 0.00181 at 153°.

used up to 100° are those of Thorpe and Rodger and for 128° and 156° the values were interpolated from the data of de Haas.

	$t_2=18$ $t_1=0$	$t_2=50$ $t_1=18$	$t_2=75$ $t_1=50$	$t_2=100$ $t_1=75$	$t_2=128$ $t_1=100$	$t_2=156$ $t_1=128$
$(\Lambda_o)_{t_2} : (\Lambda_o)_{t_1}$....	1.60	1.79	1.38	1.29	1.26	1.20
$\eta_{t_1} : \eta_{t_2}$............	1.69	1.92	1.44	1.34	1.32	1.20

It is evident that there is a parallelism in the change in the two properties, but that at all temperatures the viscosity is changing considerably more rapidly than the equivalent conductance.

Finally, attention may be called to the fact that at the highest concentration (80 milli-normal) the equivalent conductance of potassium chloride passes through a maximum value between 281° and 306°, owing to the increase in the equivalent conductance of the ions being compensated by decrease in ionization; and that of sodium chloride nearly attains such a maximum.

19. IONIZATION VALUES AND THEIR CHANGE WITH THE CONCENTRATION AND TEMPERATURE.

The percentage ionization of the two salts at the different concentrations and temperatures, obtained by dividing the values given in table 9 of the conductance at any concentration by that extrapolated for zero concentration, is shown in table 12.

TABLE 12.—*Percentage ionisation.*

Substance.	Concentration.	18°.	100°.	140°.	156°.	218°.	281°.	306°.
NaCl.......	0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	0.5	98.4	98.2	98.2	98.2	97.3	95.1	92.8
	2.0	96.7	96.4	96.2	96.2	94.9	92.3	87.5
	10.0	93.6	92.7	92.2	92.1	90.2	84.5	79.6
	80.0	85.7	83.2	82.2	81.2	77.7	69.5	62.9
	100.0	84.3	81.8	80.7	79.6	....	....	....
KCl.........	0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	0.5	98.5	....	....	....	....	....	93.3
	2.0	97.1	94.9	94.5	94.2	94.4	93.3	90.0
	10.0	94.2	91.1	....	89.7	89.8	86.9	81.2
	80.0	87.3	82.6	80.6	79.7	77.3	71.9	64.2
	100.0	86.0	81.2	79.1	78.3	....	....	....

The change of ionization with the concentration at any definite temperature does not require special discussion since the functional relation must be of a corresponding form to that between equivalent conductance and concentration, which was discussed in section 17. It will suffice to recall that the results with the two salts are satisfactorily expressed up to 156° (except at very low concentrations) by the functions $(1-\gamma)=KC^{\frac{1}{2}}$ and $(1-\gamma)=K(C\gamma)^{\frac{1}{2}}$, where γ is the conductance-ratio Λ/Λ_0 or the ionization; and also that when the function $C(1-\gamma)=K(C\gamma)^n$ is applied to the data the value of the exponent n varies at different temperatures only from 1.40 to 1.50 in the case of either of the salts. It is worthy of note that the last function may also be written in the form: $\frac{(C\gamma)^2}{C(1-\gamma)}=K(C\gamma)^m$ where m, which is equal to $2-n$, has values between 0.50 and 0.60.

It will be seen that, especially in the 80 milli-normal solution, the ionization has decreased very greatly at the higher temperatures, namely, from 86 - 87 per cent at 18° to 63 - 64 per cent at 306°; and that the decrease is becoming extremely rapid at those temperatures.

Table 12 also shows that the ionization values for the two chlorides are nearly identical at all temperatures and concentrations, the variations being irregular and sometimes in opposite directions.

20. SUMMARY.

In this article has been described the construction of a platinum-lined bomb of 124 c.cm. capacity with electrodes insulated by quartz-crystal cylinders, by means of which the conductivity and specific volume of aqueous salt solutions can be determined with an accuracy of 0.2 or 0.3 per cent, at least up to a temperature of 306°.

Measurements of the conductivity and specific volume have been made upon solutions of sodium and potassium chlorides at concentrations varying from 0.0005 to 0.1 normal, at the temperatures 100°, 140°, 156°, 218°, 281°, and 306°. Conductance values for potassium chloride at temperatures intermediate between 18° and 100° have also been presented. For the final results see table 9, page 47.

The results obtained with these salts show that even at the highest temperature the ionization calculated from the conductance-ratio does not change with the concentration in much closer accord with the requirement of the mass-action law than at the ordinary temperature. Various empirical functions which have been proposed for the expression of the change of conductance with the concentration were tested as to their applicability to the results at these widely different temperatures by a graphical method by which the effect of the uncertainty in the equivalent conductance (Λ_0) for zero concentration was eliminated. It was found that of those containing only two arbitrary constants the ones given by Kohlrausch, $\Lambda_0-\Lambda=KC^{\frac{1}{2}}$, and by Barmwater, $\Lambda_0-\Lambda=K\Lambda^{\frac{1}{2}}C^{\frac{1}{2}}$, were satisfactory at temperatures up to 156°, but that at higher temperatures there were considerable deviations between the observed and calculated values. To make applicable the general function $\Lambda_0 - \Lambda = K\Lambda^n C^{n-1}$ (of which the van't Hoff function $\Lambda_0 - \Lambda = K\Lambda\ C^{\frac{1}{2}}$ is a special case), it is necessary to vary the exponent n somewhat with the nature of the salt and with the temperature. The values of n lie, however, between 1.40 and 1.50 for both salts at all temperatures.

The conductance values extrapolated for zero concentration, and therefore the migration-velocities of the ions, were found to increase with the temperature steadily, but not uniformly. It is shown that at any rate up to 156° there is a rough parallelism between the equivalent conductance of the ions and the fluidity (reciprocal of the viscosity) of the water as determined by other workers; but that the latter increases at all these temperatures somewhat more rapidly than the equivalent conductance of completely ionized potassium chloride.

The ratio of the equivalent conductance of sodium and potassium chlorides at zero concentration decreases from 0.84 at 18° to 0.96 at 306°, showing that the migration-velocities of the sodium and potassium ions are slowly approaching relative equality.

The degrees of ionization of the two salts are nearly identical (extreme variation about 2 per cent) at all temperatures and concentrations. The ionization in 0.08 normal solution has approximately the following values: 86 per cent at 18°, 83 per cent at 100°, 80 per cent at 156°, 77 per cent at 218°, 70 per cent at 281°, and 63 per cent at 306°. It is decreasing with great rapidity at the higher temperatures. Its change with the concentration is at all temperatures accurately expressed by an equation of the form $\frac{(C\gamma)^2}{C(1-\gamma)} = K(C\gamma)^m$ in which the exponent m always has values lying between 0.50 and 0.60.

The specific volume of the 0.002 normal solutions, which can be regarded as identical with that of pure water, was found to be 1.187 at 218°, 1.337 at 281°, and 1.437 at 306°. The expansions of the two 0.1 normal solutions are substantially identical, but somewhat less than that of water, as is shown by the fact that the ratio of their specific volumes at 306° and 4° is 1.424, instead of 1.437.

PART III.

LATER MODIFICATIONS OF THE APPARATUS AND METHOD.

BY WILLIAM D. COOLIDGE.

PART III.

LATER MODIFICATIONS OF THE APPARATUS AND METHOD.

Since the work described in Part II of this publication was completed, three other bombs and various heaters have been constructed and used, and the experience gained in constructing these, and especially that gained in adapting the apparatus to use at still higher temperatures, has led to certain important modifications in the original apparatus and method, which will be here described.

21. NEW MATERIAL FOR THE SHELL OF THE BOMB.

A hot-rolled, open-hearth, low-carbon steel has been employed in the three new bombs instead of the crucible steel used in the original one. This material works much easier in the lathe and thus makes the construction of the shell easier. It is probably also better adapted to the purpose, since ductility rather than extreme tensile strength is desirable.

These bombs were all cut without forging from one bar of the steel, as was also a test piece for the determination of its coefficient of heat expansion. This last was determined in this laboratory by Mr. R. B. Sosman by means of the Abbe-Fizeau dilatometer as improved by Pulfrich.* For this purpose the specimen in the form of a ring 5 mm. thick, and of 32 mm. external and 22 mm. internal diameter, was cut out of the solid stock, taking care in machining it that the last cuts should be very light, so as not to change the properties of the steel by the mechanical treatment. Mr. Sosman found for the true coefficient of linear expansion $(\alpha = \frac{1}{l_0}\frac{dl}{dt})$ between the limits of temperature 0° and 350°:

$$10^7\alpha = 115 + 0.101\,t$$

or for the volume of the bomb (V_t) at $t°$:

$$V_t = V_0(1 + 345 \times 10^{-7}t + 0.152 \times 10^{-7}\,t^2)$$

22. SCREW-THREAD ON THE STEEL SHELL.

The ordinary thread of the form < originally used has been replaced by a thread of the form ≤, as is illustrated in fig. 9. This form of thread reduces friction, prevents the spreading of the large nut with use, which was noticeable with the ordinary thread and which, of course, weakened the bomb, and prevents the slight lifting of the cover which took place,

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*Z. Instrumentenkunde, **13**, 365, 401, 437 (1893).

due to the spreading of the large nut when the pressure came on within the bomb and when, at any stage of the heating, the large nut was heated faster than the lower part of the bomb.

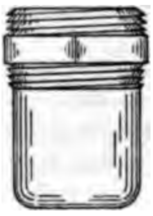

Fig. 9.

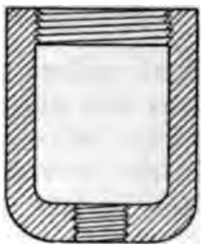

Fig. 10.

A second screw-thread of exactly the same size as the first is also cut below the hexagonal part of the steel shell, as shown in the same figure. This screws into the special chuck described in section 23, and so helps in the construction of the bomb and in the removal of the platinum lining from the shell. (See section 25.)

23. SPECIAL LATHE-CHUCK USED IN THE CONSTRUCTION OF THE BOMB.

The construction work has been greatly facilitated by the use of a special lathe-chuck. This is shown in vertical section in fig. 10. It is a cup-shaped piece of cast iron which at the lower end screws on to the spindle of the lathe. The upper end is made to take the thread on the shell of the bomb. All of the finishing of the shell, both at the top and bottom, is done with the latter screwed into this chuck, with the result that the bomb can at any time be brought into the lathe so as to run perfectly true.

24. A NEW COMPOSITE LINING FOR THE BOMB.

The original form of the platinum lining of the lower part of the bomb was, when once in place, perfectly satisfactory for work up to 306°. But for higher temperatures the lining always leaked at the curved portion near the bottom. This was doubtless due to the unequal expansion upon heating of the shell and lining. These were fastened together by the screws and packing-ring at the upper end and by the electrode at the lower end. Upon heating there was a tendency for the steel, which expands more than platinum, to draw away from the latter, leaving it unsupported at the bend. The effect of this was not evident up to 306°, but at higher temperatures it caused a very bad leak, for at these temperatures water passes freely through the pores of the platinum at any unsupported place. Moreover, there was always a great deal of difficulty in originally fitting the lining to the curved portion of the bottom, so that upon first applying the hydraulic pressure the lining often tore at this point.

These difficulties are entirely obviated by doing away with the curved portion, thus making the bottom flat, and by using a lining made in part of platinum and in part of gold. This plan is illustrated in fig. 11. *a, a* is the flange, which is now made of a platinum-iridium alloy containing 12 per cent of iridium; for this alloy is sufficiently hard for the purpose and can be rolled into the groove in the shell without the slight danger of cracking inherent in the use of the 15 per cent alloy. *b, b* is the body of the lining and is made of commercially pure platinum, which has the advantage of being somewhat more ductile than the ordinary platinum containing about 2 per cent of iridium. *c, c* is a cup of fine gold, formed by pressing a sheet of gold through a die. It is about 1 cm. high and is fused at its upper edge only to *b, b*. Its advantages over platinum are that it is more ductile and therefore easier to fit in place; that it probably does not offer so easy a passage through its pores to water at high temperature; and that its expansion-coefficient is nearly equal to that of steel, thus diminishing the difference in expansion of the lining and shell. *d* is a circular disk of platinum-iridium alloy with 15 per cent iridium, about 1.3 cm. in diameter. The use of some such hard and smooth material is imperative at this point, since otherwise the lining would become indented under the V-shaped ridge on the end of the quartz insulator, and it would then be very difficult, after the first time, to put in an electrode so that it would be tight.

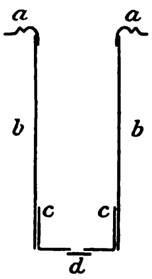

Fig. 11

The flange is still, as it was originally, soldered with fine gold to the body of the lining. The upper end of the gold cup is very easily fused to the platinum by bringing the flame of the blast lamp onto the outside of the platinum a little above the level of the cup. Before fastening the cup in place it is well to put in the platinum piece, *d*. For this purpose the gold cup is inverted, and the disk, which is about 2 mm. larger than the hole in the cup, is placed over it. The flame is then brought onto the platinum.

The thickness of the different pieces of sheet metal used in the lining is, as originally, 0.41 mm.

25. A METHOD FOR REMOVING THE LINING BY HYDRAULIC PRESSURE.

The original method for removing the lining, described in Part II, section 5, was applicable only in case the bomb had not been previously heated. In case it had been heated, no method was available for removing the lining without spoiling the flange and seriously straining the metal composing the body of the lining. But by utilizing the chuck described in section 23 the lining can at any time be readily removed without injury by a method to be now described. The same method would also be applicable to the removal of the lining from calorimetric bombs, or even to the removal of a long cylindrical platinum tube from a surrounding reinforcing tube.

The lower electrode is first removed from the bomb and replaced by the steel piece shown in fig. 3, section 5, Part II, a gold washer being placed under the V-shaped ridge to protect the lining and to make the joint tight. A hardwood piece is then turned to fit the inside of the bomb as closely as possible. The auxiliary cover shown in fig. 4 is next fastened on in the usual way, and the bomb is then screwed into the cast-iron cup, fig. 10. A hydraulic pump is now connected with the bottom of this cup and oil is forced into the space between the bomb and the cup. This oil flows through the small holes in the steel shell and presses the lining on to the hardwood piece within. A pressure of about 25 atmospheres, kept on for two or three minutes, suffices. The bomb is then taken apart, and the wooden plug with the lining on it may be readily removed. The lining is then removed from the wood by heating it until the wood is slightly charred.

26. A MORE DELICATE LEAKAGE TEST.

The original test of the lining with the hydraulic pump proved to be insufficient, as the bomb may stand this test and yet permit the escape of steam at high temperatures. The following has been found to be a much more delicate and satisfactory test:

The cover and lower part of the bomb are connected separately by means of the auxiliary pieces, figs. 6 and 4, section 5, Part II, with a cylinder of liquid carbonic acid, thus subjecting them to a gas pressure of about 50 atmospheres. Before doing this the lining must be carefully dried, best by rinsing with alcohol and ether, and it is well to insert in the bomb cavities a little absorbent cotton, to take up any trace of liquid which might be originally present in the tube connected with the carbonic acid cylinder. The part being tested is then immersed in a glass jar of xylene, or of some other colorless liquid which does not absorb carbonic acid. The position of a leak is shown by the hole in the steel shell from which the gas bubbles are seen to emerge.

27. SOLID PLATINUM-IRIDIUM ELECTRODES.

The platinum-covered steel electrodes originally used were somewhat inconvenient because of the difficulty that attended their removal. After a few experiments the brass nut, *N*, fig. 1, Part II, always got rusted on so that it could not be taken off with the wrench. This difficulty has been obviated and the construction rendered much easier by making the electrode entirely of a platinum-iridium alloy with 15 per cent iridium. This material is about as hard as steel and takes a good, strong screw-thread. Two forms of this electrode have been used. Of these, fig. 12 shows the form adapted to the inside of a quartz cup. It is made by screwing two circular disks, one 0.5 mm. thick and 15 mm. in diameter, and the other 1.6 mm. thick and 6.3 mm. in diameter, tightly onto a rod 3.17 mm. in diameter, and then soldering them together and to the rod with pure gold. The disks must be screwed on, since riveting with subsequent gold soldering does not hold. The rod is then held in the lathe-chuck while the upper portion is turned true.

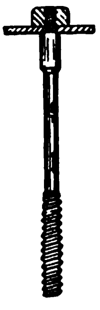

Fig. 12.

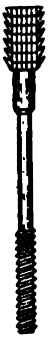

Fig. 13.

For poorly conducting solutions the quartz cup may advantageously be replaced by a plain cylinder, as this exposes less quartz surface to the action of the solution. The electrode is then given the form shown in fig. 13. As before, the rod is screwed and gold-soldered into the upper portion of the electrode. To increase its effective area this electrode is corrugated both along and at right angles to its axis, and to facilitate the escape of gas and vapor bubbles the points resulting from the cross corrugations are made to slant upwards, as shown in the figure. For the same purpose a series of concentric grooves is turned in the upper end surface.

With the use of this platinum-iridium alloy instead of steel for the electrode rod, the compensating washer, *Z*, fig. 1, has to be made of some material having a smaller coefficient of expansion than steel. Fused silica has been found entirely satisfactory for this purpose; and, as it is an electrical insulator, the mica washer *M* is no longer needed. Since fused quartz is very brittle it is necessary to make the upper portion of the nut *N* larger, so as to present a larger bearing surface on the washer. It is conveniently made from a piece of round brass rod, the lower portion being filed hexagonal to take the wrench.

It was thought that cups of fused silica might be cheaper to make than those of quartz-crystal, and this has proved to be the case. But the material is not adapted to this purpose, because of its extreme brittleness, for much more care has to be exercised in working it and the little ridges which serve to make the joints tight seem invariably to crack upon using.

28. APPARATUS AND METHOD FOR ROTATING THE BOMB IN THE HEATERS.

It was evident that for temperatures approaching the critical one, it would be necessary to provide some means for effectively stirring the solution in the bomb without removing the latter from the heating bath. This was also desirable at all temperatures. It is accomplished by rotating the bomb about a horizontal axis by the method illustrated in fig. 14. As will be evident from the diagram, the lower thread on the bomb is screwed into a steel ring *R* which is eccentrically mounted on a horizontal shaft, S_1, S_2.* The eccentricity of mounting is such that the uppermost and lowermost projections from the bomb are equidistant from the axis of the shaft, thus reducing to a minimum the size of the heating bath required to permit of rotation. The shaft is supported at the ends

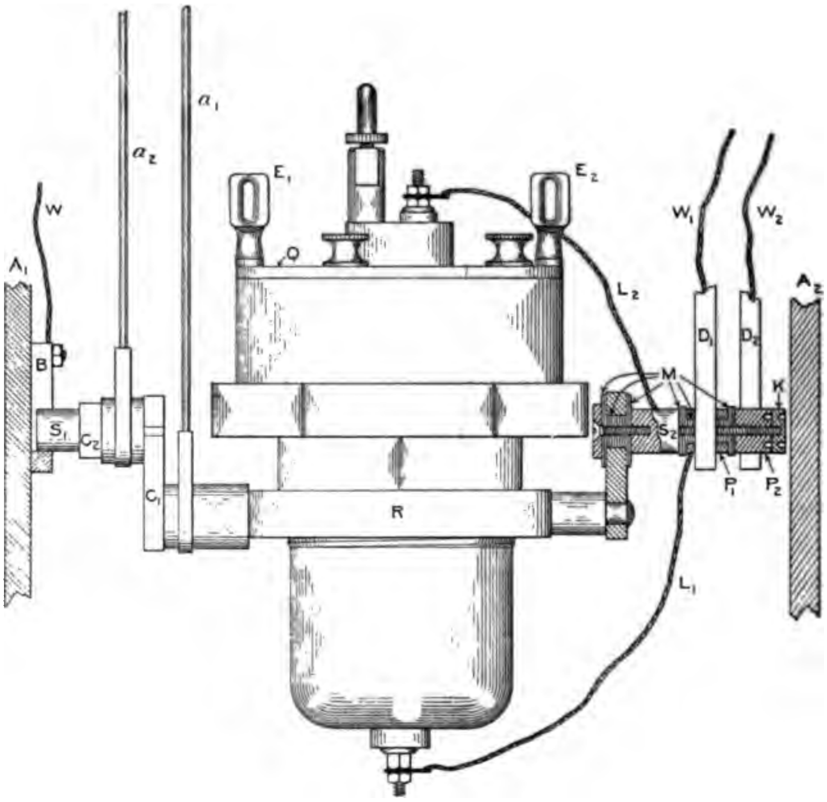

Fig. 14.

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*Because of the many joints in the steel carriage and of the temperature changes to which it is subjected, it is necessary that the joints should be riveted, not screwed, and that it should be made of the same kind of steel throughout, since otherwise it is continually loosening up.

by brass pieces bolted to the inner sides (A_1, A_2) of the bath, and is rotated by means of two cranks C_1 and C_2, at right angles to each other, and of the eccentric rods a_1 and a_2, which extend up through the cover of the bath. The ends of these rods are grasped in the fingers, and rotation is secured by alternately pulling and pushing them.

Electrical connection with the outside of the bomb is secured through the carriage, the supporting piece *B*, and the copper wire *W*, which is brazed into the latter. Connection with the lower electrode is secured through the flexible copper lead-wire L_1, the insulated steel ring P_1, into which the lead-wire is brazed, the insulated brass piece D_1, on which the ring P_1 rests, and the copper wire W_1, which is brazed into D_1; and, similarly, the upper electrode communication is through L_2, S_2, P_2, D_2, and W_2. The method of insulating P_1 from P_2 and P_2 from *R* will be clear from the diagram. In this diagram *M* denotes mica, and *K* is simply a checknut to keep the rings from turning on the shaft.

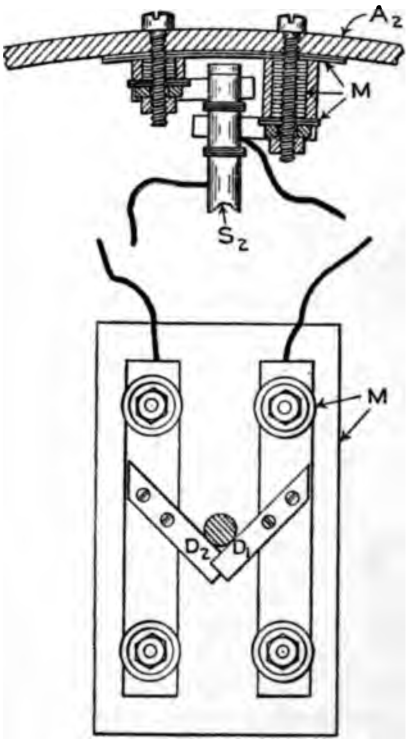

Fig. 15.

As the insulated pieces D_1 and D_2 have to support half the weight of the bomb, they, in turn, have to be securely fastened to the inner wall of the bath. The method for securing this support and at the same time insulation by means of mica is shown in fig. 15, in which the lettering is the same as in fig. 14.

To be sure of low resistance contacts the ends of the steel shaft and the brass supporting pieces must be thoroughly cleaned before the bomb is put into the bath.

For convenience in manipulation, the carriage, S_1RS_2, is supported when not in the bath, by resting the ends of the shaft in a wooden **U**-shaped stand. The bomb when ready is screwed to the carriage and the flexible lead-wires bolted to the electrodes. It can then be picked up and lowered into the bath by means of a double-pronged hook which slips into two brass eyes, E_1 and E_2, attached to diametrically opposite points of a flat brass ring, *Q*, which is fastened by means of three thumb nuts to the large nut of the bomb. The bomb is afterwards removed from the bath in the same manner, and is hung up upon the hook before a fan to cool.

29. A VAPOR BATH FOR HEATING THE ROTATING BOMB.

Such a bath is shown in vertical section in fig. 16. It is made from a piece of ordinary wrought-iron water-pipe, 23 cm. in bore and 46 cm. long. At the lower end the diameter of this pipe is reduced and a bottom is welded in. This reduction in the area of the bottom serves to diminish the amount of boiling substance needed. The cover is a thin plate of sheet iron having the edge rolled over, and sets into a groove in the top of the bath, this groove being formed by shrinking an iron ring of L-shaped cross-section onto the upper end of the pipe, which has previously been turned true on the outside for a short distance. The cover is sealed by pouring some melted Rose metal into the groove. After an experiment the cover can be raised a little out of the melted metal shortly before it solidifies, since the temperature of the bath is then so low that but little vapor would escape, even if the cover were completely removed.

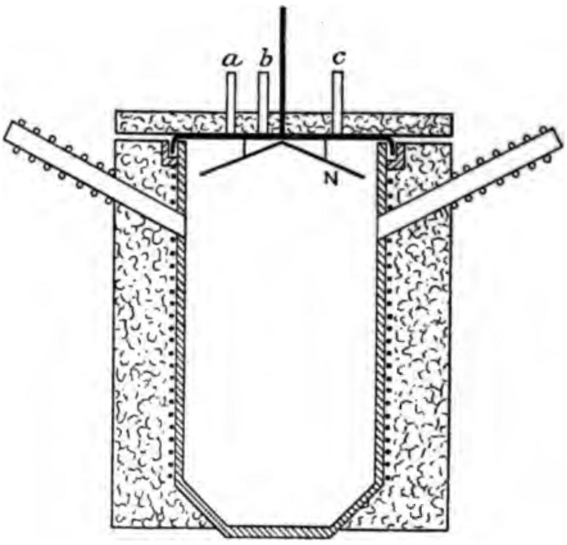

Fig. 16.

As in the earlier heaters, a loose roll of copper or iron gauze is placed in each of the condenser tubes, and, to increase still further the efficacy of these condensers, a spiral of small tubing, either of lead or seamless copper, is wound tightly around each of them and water is circulated through these spirals.

The cylindrical iron shield used in the earlier vapor baths, designated by *Q* in fig. 2, Part II, is, for various reasons, undesirable in the present bath and has been shown to be unnecessary, provided the outside of the bath is sufficiently protected from radiation. *N* is a conical shield of thin sheet iron, which is supported by three short iron rods riveted into the cover, and keeps the condensed liquid from dropping onto the bomb.

The eccentric-rods for rotating the bomb extend out through iron chimneys *a* and *b*, which are brazed into the cover. A little cotton stuck in the ends of these chimneys prevents almost completely the escape of vapor. The thermometer is similarly introduced through the chimney *c*. Of the three wires leading to the bomb, *W*, fig. 14, does not need to be insulated and is brought out through a small hole drilled in the wall of the bath near the top. The other two, W_1 and W_2, are drawn separately into asbestos tubing and then brought out through one of the condenser tubes.

There is such a large mass of metal in the bath that heating it by a burner below would be very slow; for this reason, an electrical heating coil of nickel-steel wire, 1.6 mm. in diameter, is, as shown, wound on the outside of the bath, the latter being first covered with a thin layer of mica and a single thickness of asbestos cloth. Two hundred and twenty volts, direct current, placed directly on the terminals of this coil, gives a current of about 18 amperes. To avoid possible superheating, the electric current is used only to raise the temperature of the bath, the temperature being subsequently maintained by the use of a single gas flame beneath.

The giving up of the glass cover made it no longer possible to see directly the height of the vapor level in the bath; but this was readily determined by blowing a little water from a wash bottle onto one of the condenser tubes, for there is a hissing sound only when the water strikes at or below the vapor level.

The heater is cooled by passing first compressed air and then water through a spiral of seamless copper tubing (6 mm. in bore), located a few centimeters above the bottom, and by removing the asbestos board on the top of the bath and directing a fan on the cover.

30. A LIQUID BATH FOR THE ROTATING BOMB.

This bath has been used principally for measurements at 18°, but is also adapted to those at temperatures up to 100°. It consists of a copper can, 25 cm. in diameter and 33 cm. high, with brass pieces bolted inside to the walls for supporting the bomb, just as in the vapor bath described in the preceding section. Rapid heating is provided for electrically by a heating coil wound on the outside, and a constant temperature is maintained by hand regulation of the current in a small resistance coil placed inside, just off the bottom and in direct contact with the liquid. The bath is cooled by water blown through a helix, consisting of 10 convolutions of seamless copper tubing 4 cm. in bore, which fits friction-tight inside the bath. To hold the temperature down to 18° in summer it is so arranged that the water can first be run through a few turns of lead pipe immersed in an ice bath and then delivered to the coil in the bath drop by drop through a sight feed; while for rapid cooling the water can be delivered directly from the mains to the coil in the bath. The copper can is well jacketed on the outside with an asbestos composition and is filled with commercial xylene, which is vigorously stirred by a small propeller run by an electric motor.

PART IV.

CONDUCTIVITY AND IONIZATION OF SILVER NITRATE, POTASSIUM SULPHATE, AND BARIUM NITRATE UP TO 306°, AND OF MAGNESIUM SULPHATE UP TO 218°.

By A. A. NOYES AND A. C. MELCHER.

PART IV.

CONDUCTIVITY AND IONIZATION OF SILVER NITRATE, POTASSIUM SULPHATE, AND BARIUM NITRATE UP TO 306°, AND OF MAGNESIUM SULPHATE UP TO 218°.

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31. OUTLINE OF THE INVESTIGATION.

The purpose of the present investigation was to extend the conductivity measurements already made with sodium and potassium chlorides to other di-ionic salts, to tri-ionic salts, and to di-ionic salts containing bivalent ions, so as to ascertain the behavior of salts of different types.

The new salts thus far studied are silver nitrate, potassium sulphate, barium nitrate, and magnesium sulphate. Experiments with the first three substances have been made at 18°, 100°, 156°, 218°, 281°, and 306°, while those with magnesium sulphate have been carried only up to 218° on account of the hydrolytic decomposition of the salt. At each temperature with each salt (except magnesium sulphate) the measurements were made at four concentrations, approximately 0.1, 0.05, 0.0125, and 0.002 normal. Some of the measurements on the salts previously studied by Noyes and Coolidge were repeated as an independent check on the accuracy of the results; for a new bomb and a different set of measuring instruments were used in this investigation. Incidentally an experimental study has also been made of the change of the conductance-capacity of the bomb with the temperature, as this is an instrumental factor of importance in all these investigations.

32. DESCRIPTION OF THE APPARATUS AND METHOD.

The apparatus used was similar to that employed in the previous investigation. Only such parts as are different will be described below.

THE CONDUCTIVITY VESSEL OR BOMB.

The bomb was lined only with platinum when the measurements up to 218° were made; but at the higher temperatures, it was found necessary to flow gold over the platinum in the lower part of the bomb, in order to make it perfectly tight.

The form of the bomb which will be designated "cell I" consisted of the platinum-lined steel vessel previously described, fitted with a fused silica cup, 1.45 cm. in diameter and 1.47 cm. in height, within which a flat platinum-iridium electrode 1.35 cm. in diameter was placed.

In "cell II" the fused silica cup and platinum-iridium electrode were replaced by an irregular-shaped platinum-iridium electrode, approximately

0.70 cm. in diameter and 0.35 cm. in height resting upon a vertical quartz cylinder 1.40 cm. in height, as illustrated in fig. 17.

This electrode and cylinder were afterwards replaced by a quartz cup, 1.42 cm. in diameter and 1.52 cm. in height, which formed "cell III." The electrode was 1.34 cm. in diameter.

CONDUCTIVITY MEASURING APPARATUS.

The conductivity was measured with an apparatus of the roller type described by Kohlrausch and Holborn and furnished by Hartmann and Braun. The slide-wire was calibrated by the method of Strouhal and Barus. The resistance coils were of manganine and were calibrated by comparison with standard resistances, certified by the Deutsche physikalisch-technische Reichsanstalt. A small induction coil of the ordinary form was used, a commutating switch being introduced between it and the bridge. It was shown that the mean of the two readings obtained by commutating was the same when the telephone also was commutated and when a Nernst string interrupter was used instead of the ordinary induction coil.

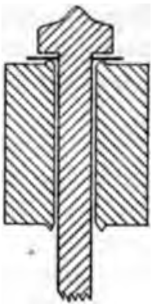

Fig. 17.

THERMOMETERS.

Three different styles of thermometers were used. The temperature of the 18° bath was determined with a 60° thermometer, reading directly to tenths, which was calibrated by comparison with a standard Baudin thermometer, certified by the Bureau of Standards of the United States. A Beckmann thermometer was used in the 100° bath; and this was calibrated immediately after each measurement by heating it in steam in a Regnault apparatus. Alvergniat 360° thermometers were used in the other baths. They were first calibrated for irregularities of bore and then at the fixed points 0°, 100°, 218°, and 306°. The values of the boiling points of naphthalene and benzophenone determined by Jaquerod and Wassmer were used throughout this whole series of investigations.

HEATERS.

Conductivity measurements were made at 18° and at about 100°, 156°, 218°, 281°, and 306°. The first of these temperatures was secured by immersing the bomb in a bath of liquid xylene contained in a well-jacketed copper cylinder. The bath could be heated electrically by passing a current through a platinum helix, or cooled by flowing cold water through a coil of lead pipe. The bath was continually stirred by a propeller, and its temperature was maintained constant to within 0.01°.

The 100° heater was a double-walled copper cylinder heated by steam. The inner cylinder was filled with liquid xylene and the bottom of the outer cylinder with water, which was heated by a coil traversed by high-pressure steam, the free steam thus produced surrounding the sides of the bath, and returning through an outside condenser to the bottom. The bomb was immersed in the liquid xylene, which was continually stirred by a propeller. The temperature was always constant to 0.01° and about 0.1° below the boiling-point of water at the prevailing pressure.

Vapor baths were used at the other temperatures. Brombenzene was used as a boiling substance for 156°, and naphthalene for 218°. The heaters were of the form described in section 3, Part II. Bromnaphthalene and benzophenone were used as boiling substances for the temperatures of 281° and 306°. The heaters used at these higher temperatures were of the rotating type described in section 29, Part III. An inverted mica cone was used to prevent the condensed vapor from dripping onto the top of the bomb.

The procedure in the conductivity measurements was essentially the same as that pursued in the previous investigation. The bomb was ordinarily rinsed thoroughly with the solution about to be used; but when a specific-volume measurement was to be combined with the conductivity measurements, the bomb was rinsed twice with alcohol and then with ether, and finally a weighed quantity of solution added. The solution was not in any case boiled to expel the air; but, before heating, the air pressure was reduced to 3 to 5 cm. mercury. In the first measurements with cell II, this was not done until after the measurement at 18°, in order to prevent the formation of air bubbles on the electrode, which could only be dislodged by shaking. The use of the rotating carriage in the later experiments allowed the pressure to be reduced before the measurement at 18° was made.

33. PREPARATION OF THE SUBSTANCES AND SOLUTIONS.

The sodium and potassium chlorides were purified by precipitation with hydrochloric acid, the latter being recrystallized from hot water. The salt was finally dried and ignited.

The potassium sulphate was purified by repeated crystallization from hot water; it was then dried and ignited.

The silver nitrate was recrystallized once from warm water and carefully dried in a current of dry air at 140°. The salt was always kept over calcium chloride in the dark. Portions of the salt were dissolved in water, the silver was precipitated as silver chloride, and the precipitate was washed and dried. The calculated percentages of silver nitrate for the first lot of salt analyzed in February, 1904, were 99.86, 100.01, and 99.88; mean 99.92. The second lot analyzed in April, 1904, gave 99.78, 99.82 and 99.89, and in July, 1905, gave 99.88 and 99.84, the mean being 99.86.

The barium nitrate used was crystallized once from hot water and carefully dried in a current of dry air at 130°. The solutions were made up by weighing out the theoretical quantities. It was proved that a portion of salt (3 grams) lost in weight scarcely appreciably (less than 0.5 mg.) on heating for 3½ hours at 280° to 300° in a platinum dish.

The magnesium sulphate was recrystallized from hot water and redissolved without drying in conductivity water to form a stock solution. This solution was analyzed separately for magnesium by precipitating it as magnesium ammonium phosphate and for sulphate by precipitating it as barium sulphate. The content in 1,000 grams of solution expressed in milli-equivalents (1 milli-equivalent = 60.21 mg. $MgSO_4$) was found to be as follows:

From magnesium determination	344.9
From sulphate determination	345.1
From sulphate determination	344.6
Average	344.9

The solutions of all these substances were made up by weighing out the dry salt, or the stock solution in the case of magnesium sulphate, transferring to a graduated flask, and adding conductivity water enough to bring the solution to the graduation mark at some known temperature between 15° and 25°. The concentration of the salt was then calculated over to 4° on the assumption that the solution had the same expansion-coefficient as pure water.

34. SYSTEMATIC ERRORS AND THEIR ELIMINATION.

VOLATILIZATION OF THE SOLVENT.

The vapor space in the bomb at the temperatures 100°, 156°, and 218° was not sufficiently large to cause an error of 0.1 per cent; and no correction was applied at these temperatures. However, at 281° and 306°, it was necessary to apply a correction, which varied with the amount of liquid in the bomb. The vapor-space correction at 281° was determined experimentally by measuring the conductance when two different quantities of a 0.01 normal sodium chloride solution were introduced.

The results were as follows:

Grams of solution.	Volume at 281° of		Conductance of solution.
	Solution.	Vapor-space.	
91.5	121.4	1.6	20606
60.9	78.9	44.1	21107

By calculation* from these data, the specific volume of water-vapor at 281° was found to be 29. That at 306° was found to be 18 by plotting the previously known values up to 200°, this value at 281°, and that at the critical temperature. In all the experiments of this investigation the volume of the vapor-space at 306° was determined by measuring the ratio of the conductances at the upper and lower electrodes at 306°, and that at 281° was calculated from this with the help of the ratio of the specific volumes at 281° and 306° and the volume of the bomb at those temperatures.

From the specific volumes of vapor and solution and the actual volumes of the vapor-space and of the solution the corrected concentration (C_0) was calculated from that (C) which would have prevailed if there had been no vaporization.† The correction was on an average +0.43 per cent at 281° and +0.13 per cent at 306°.

CONDUCTANCE OF THE WATER.

The conductance of the water was experimentally determined by making measurements with conductivity water at the different temperatures by exactly the same procedure as was followed with solutions. It was subtracted from the conductance of the solution in every case. The necessary data will be found in section 35.

CONDUCTANCE-CAPACITY IN RELATION TO THE VOLUME OF SOLUTION IN THE BOMB.

The following experiment was made in order to determine whether the conductance-capacity of the bomb was at all affected by such variations in the volume of the solution contained in it as actually occurred in this investigation. Different quantities of 0.01 normal potassium chloride solution were put into the bomb and measurements made at both 18° and approximately 100°.

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*This was done by means of the equation $v = 2\frac{L_4 + L_8}{L_4 - L_8}\left(\frac{v_1}{w_1} - \frac{v_2}{w_2}\right)$ in which v is the specific volume of the vapor, v_1 and v_2 represent the vapor-spaces, w_1 and w_2 the weights of solution, and L_4 and L_8 the conductances in the two experiments.

†This was done by means of the equation $C_0 = C\left(1 + \frac{v_1/v}{\frac{V_1}{V} + \frac{v_1}{v}}\right)$ in which V and v are the specific volumes of the liquid and vapor respectively, V_1 and v_1 are the actual volumes of the liquid and vapor respectively.

The results were as follows:

Cell No.	Weight of solution.	Temperature.	Conductance.
II	113.25	18.00	3992.0
		99.88	11824
II	56.80	18.00	3993.8
		99.88	11828

It will be seen that the difference in conductance is insignificant at both temperatures, although in one experiment the bomb was less than half full of liquid. A computation shows in fact that the volatilization of solvent at 100° would be such as to account almost exactly for even the slight difference of conductance observed at that temperature. Therefore, no correction for change in conductance-capacity from variation in the quantity of liquid was required in any of the measurements made in this investigation.

35. THE CONDUCTANCE-CAPACITY AND THE WATER CORRECTION.

The conductance-capacity of the cells was computed from conductivity measurements made at 18° with various solutions of potassium and sodium chlorides, using for the equivalent conductances of the solutions the values of Kohlrausch and Maltby.* The data are given in table 13.

The final values of the conductance-capacity were used in calculating the equivalent conductance in all experiments made on or between the dates on which the corresponding separate values were determined. Between the last date of one set and the first date of a following one, intermediate values of the conductance-capacity were used, the value being varied in accordance with the probable changes caused by the successive runs. The value at 18° actually used in each experiment will be given in connection with the conductivity data for that experiment (section 39). In the experiments which were carried to 281° and 306°, the conductance-capacity at 18° after heating was often appreciably different from that at the beginning; and in such cases the values used at 281° and 306° were based upon the *final* conductance-capacity at 18°. In presenting the data of these experiments the separate values of the conductance-capacity at each temperature will be given in the tables.

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*Wissensch. Abhandl. phys.-techn. Reichsanstalt, **3**, 210. See also Landolt-Börnstein-Meyerhoffer, Tabellen, p. 744.

TABLE 13.—*Conductance-capacity—Data and final values.*

Date.	Cell No.	Salt.	Milli-equivalents per liter at 18°.	Conductance × 10^6.	Conductance-capacity.	
					Separate values.	Final values.
1904						
Jan. 11 ...	I	KCl	10.00	1365.3	0.8972	......
Jan. 22 ...	I	"	20.00	2673.1	0.8977	0.8974
Mar. 25 ...	I	KCl	10.00	1366.9	0.8962	......
Mar. 28 ...	I	"	100.00	12499	0.8965	......
Mar. 30 ...	I	NaCl	10.00	1138.5	0.8962	......
Apr. 1 ...	I	"	100.00	10278	0.8954	0.8960
May 10 ...	I	KCl	1.999	283.9	0.8920	......
May 10 ...	I	NaCl	2.500	295.7	0.8920	......
May 11 ...	I	"	10.00	1144.4	0.8917	0.8919
June 16 ...	II	NaCl	20.00	6304.4	0.3163	......
June 16 ...	II	KCl	20.00	7576.8	0.3167	0.3165
June 29 ...	II	NaCl	10.00	3326.4	0.3070	......
June 29 ...	II	KCl	10.00	3991.7	0.3071	......
June 30 ...	II	NaCl	2.497	857.7	0.3070	......
July 1 ...	II	"	10.00	3325.4	0.3070	0.3070
1905						
Mar. 13 ...	II	KCl	10.01	4122.2	0.2974	......
Mar. 14 ...	II	"	10.01	4121.8	0.2974	......
Mar. 15 ...	II	NaCl	10.01	3433.9	0.2975	......
Mar. 17 ...	II	"	10.00	3429.4	0.2975	......
Mar. 18 ...	II	"	10.01	3432.9	0.2975	......
Mar. 21 ...	II	"	10.01	3431.2	0.2974	......
Mar. 23 ...	II	"	10.00	3429.8	0.2974	......
Mar. 29 ...	II	"	9.96	3419.6	0.2974	0.2974
Apr. 24 ...	II	KCl	10.00	4150.6	0.2951	......
Apr. 25 ...	II	NaCl	10.00	3459.6	0.2950	0.2950
May 10 ...	II	"	10.00	3499.1	0.2917	0.2917
May 15 ...	II	"	10.00	3526.3	0.2894	0.2894
May 18 ...	II	"	10.00	3536.2	0.2885	......
May 18 ...	II	KCl	10.00	4247.6	0.2884	0.2885
May 23 ...	II	"	10.00	4247.6	0.2884	0.2884
July 18 ...	II	NaCl	10.00	3502.6	0.2913	0.2913
Sept. 26 ...	III	"	100.00	8045.7	1.1438	......
Sept. 27 ...	III	KCl	99.99	9779.9	1.1454	1.1446
Oct. 1 ...	III	NaCl	100.04	8072.3	1.1406	......
Oct. 2 ...	III	KCl	100.06	9818.3	1.1418	1.1412
Oct. 9 ...	III	"	100.04	9875.6	1.1349	1.1349
Oct. 27 ...	III	"	99.91	9947.2	1.1252	1.1252
Nov. 20 ...	IV	"	19.963	1968.9	1.2164	......
Nov. 21 ...	IV	"	9.982	1003.6	1.2183	......
Nov. 25 ...	IV	"	99.88	9185	1.2183	......
Nov. 28 ...	IV	NaCl	99.89	7540	1.2192	1.2181

Measurements of the conductance of the water, such as was used in making up the solutions, were made at the various temperatures, observing the same order and times of heating at each temperature as prevailed in the experiments with the salt solutions. The bomb was always previously freed from adsorbed substance by two or three heatings of an hour each with water at 218° or 306°. The actual conductances measured in the bomb multiplied by 10^6 are given in table 14. The appropriate mean of these values was always subtracted from the conductance of the solution.

TABLE 14.—*Actual conductance of water in the bomb.*

Date.	Cell No.	18°		100°		156°		218°
		Initial.	Final.	Initial.	Final.	Initial.	Final.	
1904								
Jan. 6	I	0.77	1.42	2.86	4.74	5.22	6.38	7.87
Jan. 7	I	0.79	2.62	4.14	7.72	8.34	9.91	10.48
Jan. 8	I	0.97	2.56	3.49	6.16	5.90	7.65	8.56
Feb. 10	I	0.69	3.20	3.73	8.70	7.18	10.99	11.73
Feb. 11	I	0.92	2.67	3.52	7.02	6.16	8.93	10.38
Apr. 21	I	0.76	1.47	2.77	3.52	5.10	5.71	7.76
Apr. 22	I	0.76	1.88	2.74	4.71	4.38	5.71	7.08
May 17	I	0.86	1.73	3.73	4.49	6.12	6.84	9.05
May 18	I	0.86	3.63	3.52	8.23	5.49	8.11	10.00(?)
Mean	I	0.82	2.36	3.49	6.14	5.99	7.80	9.11
July 14	II	2.25	3.68	8.93	11.3	14.9	17.8	22.8
July 23	II	2.46	6.61	8.93	17.1	15.5	22.2	23.6
Mean	II	2.36	5.14	8.9	14.2	15.2	20.0	23.2
				281°	306°			
July 14	II	2.25	....	58.0	58.0	....	....	....
July 25	II	3.31	10.4	37.9	48.0	....	....	....
July 27	II	2.25	11.4	27.1	29.0	....	....	....
1905								
Feb. 15	II	2.04	5.5	48.8	52.7	....	....	....
Feb. 16	II	2.04	7.3	51.7	56.7	....	....	....
Mean	II	2.40	8.6	44.7	48.9	....	....	....

36. VARIATION OF THE CONDUCTANCE-CAPACITY WITH THE TEMPERATURE.

The following measurements and computations were made in order to determine what variation in the conductance-capacity of the bomb is caused by the change in the diameter and length of the electrode cup or of the small electrode and in the diameter of the bomb itself owing to the expansion upon heating.

The apparatus used to determine the variation of the conductance when the electrode was placed within the quartz cup was an imitation of the bomb, consisting of an outer cylindrical brass vessel, a cup composed of a glass tube with a brass electrode permanently fixed at the bottom of the tube with rosin, and a piece of insulating material (the "red fiber" of trade) separating the cup from the bottom of the vessel, and allowing the electrode rod to pass through it. Combinations of three such electrode cups of diameters 1.31, 1.50, and 1.59 cm. and of two brass vessels of diameters 4.22 and 4.54 cm. were investigated. Mercury was used to change the effective height of the cup, the change being determined by introducing weighed portions of mercury into the cup and measuring by a cathetometer the height of its surface above the electrode and below the top of the cup. The heights of the mercury in the cup were plotted against the weights of mercury, the points being found to lie on a straight line; and by means of these plots, the effective height of the cup in the succeeding experiments was derived from the weight of mercury introduced. The relative conductance at various heights was then determined by measuring that of a 0.01 normal sodium chloride solution at 18° in the apparatus, which was made up of the three electrode cups in succession and one of the brass cylinders, successive portions of mercury being added.

The effective heights of the cup were first plotted against the conductances. The diameters of the three cups were then plotted against the conductances obtained for various definite heights from the first plot. From these plots, the ratio of the fractional change in conductance ($\delta L/L$) to that in height ($\delta h/h$) for a given diameter or to that in diameter ($\delta d/d$) for a given height could be found. The results so derived for a series of heights and diameters expressed in centimeters are given in table 15. The columns headed I show the values of the ratio $\frac{\delta L/L}{\delta h/h}$ and those headed II, the values of the ratio $\frac{\delta L/L}{\delta d/d}$

TABLE 15.—*Change in conductance-capacity with the dimensions of the electrode cup.*

Height.	Diameter.							
	1.30		1.40		1.50		1.60	
	I.	II.	I.	II.	I.	II.	I.	II.
1.0	0.70	1.92	0.72	1.80	0.72	1.72	0.72	1.64
1.2	0.71	1.79	0.74	1.76	0.73	1.75	0.73	1.72
1.4	0.73	1.66	0.77	1.73	0.76	1.80	0.74	1.71
1.6	0.75	1.54	0.79	1.70	0.79	1.82	0.75	1.80
1.8	0.80	1.47	0.80	1.60	0.80	1.92	0.76	1.88
2.0	0.88	1.60	0.81	1.64	0.80	1.87	0.78	2.04
2.2	0.95	1.75	0.88	1.67	0.82	1.91	0.81	2.00

The apparatus for determining the variation of the conductance when no cup was used was made up as follows. The top of the main body of the bomb was covered with a brass disk. Through the center of this disk was inserted a hollow rod of vulcanite of the length and diameter of the quartz cylinder supporting the lower electrode in the bomb itself. Through this vulcanite tube a brass rod was inserted, which could be forced down successively so as to produce an electrode of varying length. The conductance of a 0.01 normal sodium chloride solution between this electrode and the sides of the bomb was determined. Brass electrodes of three different diameters (0.475, 0.72, and 0.95 cm.) were used.

The lengths of the electrode were plotted against the conductances for the three diameters and the diameters of the electrode against the conductances for the different lengths. From these plots, the ratio of the fractional change in conductance to that in length for a given diameter or to that in diameter for a given length can be computed. The values of the ratios so derived for a series of lengths and diameters are given in table 16, those of $\frac{\delta L/L}{\delta l/l}$ in the columns headed I and those of $\frac{\delta L/L}{\delta d/d}$ in the columns headed II.

Table 16.—*Change in conductance-capacity with the dimensions of the electrode.*

Length.	Diameter.					
	0.5		0.7		0.9	
	I.	II.	I.	II.	I.	II.
0.5	....	0.7	....	0.95	....	1.05
1.0	0.65	0.65	0.6	0.8	0.55	0.95
1.5	0.3	0.55	0.3	0.7	0.3	0.9
2.0	0.2	0.5	0.2	0.7	0.2	0.9
2.5	0.15	0.55	0.1	0.7	0.1	0.9
3.0	0.1	0.55	0.1	0.7	0.1	0.9

The variation in the conductance due to a change in diameter of the large cylindrical vessel was determined in the presence and absence of a cup by measuring the conductance of a 0.01 normal sodium chloride solution between the small electrode and brass cylinders (diameters of 3.66, 3.35, 2.39, and 1.75 cm.) placed successively inside of the outer cylinder. The effect of the increase of diameter of the bomb which would occur even up to 400° on the conductance-capacity was less than 0.1 per cent.

The linear expansion coefficients (dl/l_0dt) used in computing the change in conductance-capacity of the bombs were as follows:

	dl/l_0dt	Remarks.
Platinum-iridium electrodes	8.9×10^{-6}	Fizeau, Compt. Rend., **68**, 1125 (1869).
Quartz (length)	9×10^{-6}	Randall, Phys. Rev., **20**, 10 (1905).
Quartz (diameter)	16×10^{-6}	Benoit, Trav. et mém. Bur. Int. Poids et Mes., **6**, 190 (1888). Le Chatelier, Compt. Rend., **108**, 1046 (1889).
Steel	13×10^{-6}	See section 21, Part III.

TABLE 17.—*Specific volume—Data and final values.*

Date.	Salt.	Milli-equivalents per liter at 4°.	Temperature, $t°$.	Weight of solution.	Volume uncorrected.	Specific volume at $t°$.	Specific volume at 4°.	Specific volume ratio.
1904								156°/4°
Feb. 25..	$AgNO_3$	25	155.6	108.61	118.31	1.0917	0.9963	1.0962
Feb. 25..	$AgNO_3$	100	155.8	111.36	119.94	1.0794	0.9861	1.0948
Mar. 24..	K_2SO_4	100	156.6	110.19	119.64	1.0881	0.9933	1.0948
Apr. 13..	$Ba(NO_3)_2$	100	155.5	110.35	119.38	1.0849	0.9899	1.0957
Apr. 28..	$MgSO_4$	100	156.2	110.09	119.52	1.0880	0.9939	1.0944
								218°/4°
Mar. 29..	$NaCl$	10	218.2	100.83	118.80	1.1837	0.9996	1.1837
Mar. 29..		10	218.3	100.77	118.77	1.1841	"	1.1839
Mar. 30..		10	218.4	100.93	118.98	1.1843	"	1.1840
Mean ..	....	....	....	....	....	....	....	1.1839
Mar. 25..	KCl	10	218.4	100.80	118.79	1.1839	0.9995	1.1838
Mar. 28..	KCl	100	218.0	101.57	118.96	1.1766	0.9954	1.1820
Feb. 18..	$AgNO_3$	25	218.6	101.31	119.14	1.1814	0.9963	1.1846
Feb. 23..		25	217.6	101.06	118.65	1.1791	"	1.1846
Feb. 24..		25	216.8	101.21	118.73	1.1785	"	1.1850
Mean ..	....	....	....	....	....	....	....	1.1847
Feb. 4...	$AgNO_3$	100	218.1	101.96	118.26	1.1652	0.9861	1.1815
Feb. 5...		100	218.1	102.65	119.08	1.1654	"	1.1816
Apr. 16..		100	217.3	102.48	118.70	1.1636	"	1.1814
Mean ..	....	....	....	....	....	....	....	1.1815
Mar. 18..	K_2SO_4	50	217.7	100.96	118.48	1.1790	0.9967	1.1835
Mar. 21..		50	218.5	101.24	118.98	1.1807	"	1.1836
Mean ..	....	....	....	....	....	....	....	1.1836
Mar. 22..	K_2SO_4	100	218.4	101.28	118.27	1.1732	0.9933	1.1802
Mar. 23..		100	218.1	101.22	118.13	1.1724	"	1.1801
Mean ..	....	....	....	....	....	....	....	1.1802
Apr. 12	$Ba(NO_3)_2$	100	217.3	101.92	118.59	1.1689	0.9899	1.1821
Apr. 13		100	217.5	102.31	119.04	1.1689	"	1.1818
Mean ..	....	....	....	....	....	....	....	1.1820
Apr. 28..	$MgSO_4$	100	218.2	102.89	120.27	1.1743	0.9939	1.1812
May 2...	$MgSO_4$	200	218.4	102.68	119.26	1.1671	0.9880	1.1808
1905								306°/4°
Oct. 1...	$NaCl$	100	305.6	85.61	119.97	1.4152	0.9958	1.4228
Oct. 2...	KCl	100	305.7	85.57	119.85	1.4145	0.9954	1.4222
Nov. 20..	$AgNO_3$	50	306.0	85.38	119.62	1.4149	0.9929	1.4252
Sept. 29..	K_2SO_4	50	305.5	84.97	119.62	1.4217	0.9967	1.4284
Sept. 29..		50	305.5	85.11	119.93	1.4227	"	1.4294
Mean ..	....	....	....	....	....	....	....	1.4289
Sept. 30..	K_2SO_4	100	305.7	85.92	120.25	1.4130	0.9933	1.4237
Sept. 30..		100	305.4	85.67	119.77	1.4122	"	1.4242
Mean ..	....	....	....	....	....	....	....	1.4240
Oct. 2.	$Ba(NO_3)_2$	50	305.2	85.28	119.59	1.4165	0.9950	1.4271
Oct. 12		50	305.5	85.04	119.31	1.4174	"	1.4265
Mean ..	....	....	....	....	....	....	....	1.4268

37. THE SPECIFIC-VOLUME DATA.

The results of the specific-volume measurements are given in table 17. The first four columns need no further explanation. The fifth column gives the number of grams of solution which were weighed into the dry bomb at the start. The sixth column gives the volume expressed in cubic centimeters which, at the temperature of 100° (at which the volume of the bomb was determined) corresponds to the observed ratio of the conductances at the upper and lower electrodes. This volume was obtained by interpolation from a plot made as described in section 8, Part II. The actual volume occupied by the solution at the higher temperature is greater than this by an amount equal to the expansion of the bomb upon heating from 100° to that temperature. The temperature-coefficient of volume expansion of the steel shell of the bomb is assumed to be 0.000038 per degree, upon the basis of determinations made by R. B. Sosman in this laboratory. The seventh column gives the specific volume of the solution at the temperature of observation. It is obtained by dividing the values of the preceding column, after correcting them for the expansion of the bomb as just described, by the weight of solution given in the fifth column. The eighth column gives the values of the specific volumes at 4° of the various solutions used. The last column gives the ratio of the specific volume at the round temperatures 218°, 281°, and 306°, to that of the same solution at 4°. Thus, this ratio shows the volume occupied by that quantity of solution which at 4° has a volume of 1 c.cm. The values are obtained from those of the preceding column by reducing them to these temperatures by means of the temperature-coefficient obtained from our specific-volume values, and then dividing the results by the specific volumes of the solutions at 4°.

38. SUMMARY OF THE SPECIFIC-VOLUME VALUES.

The final values of the ratio of the specific volume at various temperatures to that at 4° are summarized in table 18. For comparison the values obtained by Noyes and Coolidge (section 12, Part II) for a 2 milli-normal solution of sodium chloride, which are substantially identical with those of pure water, are given in the table within parentheses. For the 100 milli-normal solution of this substance they found 1.187 at 218° in fair agreement with our value and 1.423 at 306° in complete agreement with our value. A comparison of values for the different 50 milli-normal solutions shows that these all expand considerably less than water itself, the ratio being 1.425 – 1.429 instead of 1.437 at 306°. Up to 218° the expansions of even the 100 milli-normal solutions of all the different salts are substantially equal (ratio 1.180 – 1.182); but at 306° the ratios for silver nitrate and barium nitrate, the salts of the metals with high atomic weights, are somewhat smaller than those for the other three salts, being 1.426 instead of 1.429 at 50 milli-normal.

TABLE 18.—*Ratio of specific volume at various temperatures to that at 4°.*

Salt.	Concentration at 4°.	Specific volume ratio.		
		156°.	218°.	306°.
NaCl.....	2	......	(1.187)	(1.437)
	10	......	1.184	......
	100	......	......	1.423
KCl......	10	......	1.184	......
	100	......	1.182	1.422
$AgNO_3$...	25	1.096	1.185	......
	50	......	......	1.425
	100	1.095	1.182	......
K_2SO_4....	50	......	1.184	1.429
	100	1.095	1.180	1.424
$Ba(NO_3)_2$.	50	......	......	1.427
	100	1.096	1.182	......
$MgSO_4$...	100	1.094	1.181	......

39. THE CONDUCTIVITY DATA.

Table 19 contains the conductivity data obtained in the separate experiments. The first column contains the date; the second, the cell-number which by reference to section 32 shows the modification of the conductivity-vessel used; the third, the concentration at 4° in milli-equivalents per liter, the international atomic weights for 1905 being employed, and the fourth, the true temperature ($t°$) of the measurement upon the hydrogen-gas scale. The fifth gives the concentration at the temperature of the measurement obtained from that at 4° by dividing it by the appropriate specific volume ratio taken directly from table 18 or derived from the values there given by linear interpolation and by correcting it (at 281° and 306°) for the solvent in the vapor-space as described in section 34. The sixth column contains the actual conductance in reciprocal ohms of the solution in the bomb, which was obtained by correcting the observed conductance for the resistance of the lead-wires and for errors in the resistance coils and slide wire. The seventh column gives the corresponding conductance-capacity of the vessel, determined as described in sections 35 and 36; when no number or quotation mark is inserted it is to be understood that the value used was the same as that given for the same temperature in the preceding experiment. The eighth column gives the equivalent conductance in reciprocal ohms, which was computed by subtracting from the actual conductance $\times 10^6$ (given in the sixth column) that of the water (as given in section 35), multiplying the remainder by the conductance-capacity (given in the seventh column), and dividing by the concentration at $t°$ (given in the fifth column).

TABLE 19.—*The conductivity data.*

SODIUM CHLORIDE.

Date.	Cell No.	Concentration at 4°.	Temperature, t°.	Concentration at t°.	Conductance × 10^6.	Conductance capacity.	Equivalent conductance.
1905 Mar. 25...	II	2.000	18.00	1.997	712.8	0.2974	105.71
			305.2	1.397	4,621.5	0.2965	970.3
			18.00	1.997	721.8	0.2974	106.22
Nov. 13...	IV	2.006	18.00	2.004	174.2	1.2181	105.5
			99.92	1.924	554.9	1.2162	349.1
			18.00	2.004	174.4	1.2181	105.5
1904 Mar. 31...	I	10.013	18.00	10.000	1,139.4	0.8960	102.02
			218.3	8.433	6,523.2	"	692.1
			18.00	10.000	1,140.8	"	102.01
July 1...	II	10.020	18.00	10.007	3,325.4	0.3070	101.96
			217.6	8.446	18,973	0.3064	687.2
			18.00	10.007	3,333.3	0.3070	102.12
1905 Mar. 15...	II	10.027	18.00	10.014	3,433.9	0.2974	101.91
			280.4	7.543	21,120	0.2966	828.6
			306.0	7.000	20,818	0.2965	879.8
			18.00	10.014	3,435.2	0.2974	101.89
Mar. 17...	II	10.009	18.00	9.996	3,429.4	......	101.96
			280.2	7.534	21,250	......	834.8
			305.8	6.989	20,943	......	886.4
			18.00	9.996	3,461.9	......	102.86
Mar. 21...	II	10.021	18.00	10.009	3,432.9	......	101.93
			279.5	7.554	21,222	......	831.5
			306.0	6.994	20,900	......	884.0
			18.00	10.009	3,473.0	......	103.07
Mar. 23...	II	10.015	18.00	10.002	3,429.8	......	101.94
			280.5	7.529	21,217	......	834.0
			306.0	6.989	20,871	......	883.4
			18.00	10.002	3,439.8	......	102.14
Mar. 29...	II	9.974	18.00	9.961	3,419.6	......	102.02
			276.5	7.571	21,119	......	825.5
			305.6	6.971	20,844	......	884.5
			18.00	9.961	3,423.0	......	102.07
April 25..	II	10.017	18.00	10.004	3,459.6	0.2950	101.94
			281.1	7.524	21,460	0.2942	837.4
			305.5	7.003	21,145	0.2941	886.1
			18.00	10.004	3,463.2	0.2950	101.98
1904 April 1 ..	I	100.13	18.00	100.00	10,284	0.8960	92.14
			218.1	84.35	55,365	"	588.2
			18.00	100.00	10,290	"	92.18
1905 Sept. 26..	III	100.13	18.00	100.00	8,045.7	1.1446	92.08
			218.2	75.64	45,147	1.1381	679.0
			305.6	70.60	43,105	1.1375	694.2
			18.00	100.00	8,058.6	1.1446	92.22
Oct. 1 ...	III	100.17	18.00	100.04	8,072.3	1.1411	92.07
			218.3	75.62	45,271	1.1346	679.1
			305.6	70.56	43,149	1.1340	693.2
			18.00	100.04	8,091.3	1.1411	92.34
Nov. 28..	IV	100.02	18.00	99.88	7,540	1.2181	91.94
			100.00	95.89	23,403	1.2162	296.8
			140.0	92.59	30,817	1.2152	404.5
			156.0	91.10	33,411	1.2148	445.5
			18.00	99.88	7,546	1.2181	92.01

TABLE 19.—*The conductivity data*—Continued.

POTASSIUM CHLORIDE.

Date.	Cell No.	Concentration at 4°.	Temperature, t°.	Concentration at t°.	Conductance × 10^6.	Conductance capacity.	Equivalent conductance.
1904							
Mar. 25 ..	I	10.015	18.00	10.002	1,366.9	0.8960	122.38
			218.4	8.433	7,048.2	“	748.0
			18.00	10.002	1,371.8	“	122.68
1905							
Mar. 13 ..	II	10.021	18.00	10.008	4,122.2	0.2974	122.40
			306.1	6.990	22,105	0.2965	935.6
Mar. 14...	II	10.021	18.00	10.008	4,121.8	0.2974	122.40
			280.6	7.510	22,550	0.2966	888.9
			18.00	10.008	4,124.0	0.2974	122.41
April 24..	II	10.008	18.00	9.995	4,150.6	0.2950	122.45
			281.3	7.512	22,750	0.2942	888.4
			305.8	6.989	22,285	0.2941	935.2
			18.00	9.995	4,154.7	0.2950	122.51
1904							
Mar. 28 ..	I	100.13	18.00	100.00	12,498	0.8960	111.98
			218.0	84.36	60,049	“	637.7
			18.00	100.00	12,522	“	112.18
1905							
Sept. 27..	III	100.12	18.00	99.99	9,779.9	1.1446	111.95
Oct. 2 ..	III	100.20	18.00	100.06	9,818.3	1.1411	111.97
			281.4	75.61	48,328	1.1346	725.0
			305.7	70.55	45,815	1.1340	736.1
			18.00	100.06	9,840.5	1.1411	112.20
Oct. 27 ..	III	100.04	18.00	99.91	9,947.2	1.1252	112.03
			281.4	75.42	49,193	1.1187	729.9
			18.00	99.91	9,978.0	1.1252	112.35
Nov. 18 ..	IV	2.002	18.00	2.000	208.2	1.2181	126.4
			25.00	1.997	240.7	1.2179	146.4
			100.00	1.920	623.1	1.2162	393.3
			140.0	1.854	818.4	1.2152	534.2
			156.0	1.824	888.3	1.2148	589.1
			18.00	2.000	208.5	......	126.2
Nov. 21 ..	IV	9.996	18.00	9.982	1,003.6	......	122.4
			25.00	9.967	1,158.6	......	141.5
			50.00	9.879	1,747.6	1.2174	215.3
			75.00	9.746	2,366.3	1.2168	295.4
			100.00	9.583	2,978.8	......	377.7
			128.0	9.355	3,632.4	1.2155	471.8
			155.9	9.104	4,219.4	......	562.7
			18.00	9.982	1,004.5	......	122.5
Nov. 20 ..	IV	19.992	18.00	19.963	1,968.9	......	120.1
			25.00	19.933	2,271.1	......	138.8
			50.02	19.756	3,415.3	......	210.4
			100.00	19.165	5,803.8	......	368.3
			18.00	19.963	1,968.3	......	120.1
Nov. 25...	IV	100.01	18.00	99.87	9,185	......	112.0
			25.00	99.72	10,562	......	129.0
			50.00	98.83	15,810	......	194.7
			75.02	97.51	21,245	......	265.1
			100.00	95.88	26,546	......	336.7
			128.0	93.60	32,123	......	417.1
			140.0	92.58	34,270	......	449.7
			156.0	91.09	36,957	......	492.8
			18.00	99.87	9,183	......	112.0

TABLE 19.—*The conductivity data*—Continued.

SILVER NITRATE.

Date.	Cell No.	Concentration at 4°.	Temperature, t°.	Concentration at t°.	Conductance × 10^6.	Conductance capacity.	Equivalent conductance.
1904 Feb. 16...	I	1.999	18.00	1.997	250.20	0.8974	112.02
			99.67	1.917	752.45	"	350.7
			155.4	1.822	1,083.7	"	530.9
			217.6	1.685	1,363.0	"	720.9
			155.5	1.822	1,092.7	"	534.5
			99.69	1.917	759.36	"	352.6
			18.00	1.997	254.52	"	113.35
Feb. 17...	I	1.999	18.00	1.997	250.34	......	112.14
			99.97	1.916	755.07	......	352.0
			155.7	1.821	1,087.4	......	532.8
			218.3	1.684	1,362.4	......	721.4
			155.8	1.821	1,091.4	......	534.0
			99.97	1.916	761.50	......	353.8
			18.00	1.997	253.50	......	112.89
June 27...	II	2.002	18.00	1.999	733.31	0.3070	112.25
			99.88	1.919	2,199.9	0.3068	305.2
			155.5	1.824	3,182.6	0.3066	532.2
			217.8	1.687	4,039.8	0.3064	729.0
			155.6	1.824	3,201.4	0.3066	534.6
			99.88	1.919	2,221.8	0.3068	352.8
			18.00	1.999	742.17	0.3070	113.18
1905 May 19...	II	2.000	18.00	1.997	782.9	0.2884	112.62
			280.3	1.503	4,719.9	0.2876	894.2
			304.8	1.399	4,692.6	0.2875	953.9
			18.00	1.997	817.3	0.2884	117.31
May 22 ..	II	1.996	18.00	1.994	479.9	......	112.38
			280.8	1.499	4,707.0	......	894.8
			305.5	1.394	4,666.4	......	952.4
			18.00	1.994	805.2	......	115.75
May 23...	II	1.999	18.00	1.996	478.8	......	112.10
			281.0	1.500	4,699.0	......	892.8
			305.5	1.395	4,665.7	......	951.4
			18.00	1.996	803.0	......	115.30
July 11..	II	2.004	18.00	2.002	774.83	0.2913	112.32
			305.7	1.398	4,662.9	0.2904	956.0
			18.00	2.002	820.75	0.2913	118.20
April 14...	I	12.481	18.00	12.47	1,497.5	0.8958	107.55
			99.84	11.97	4,476.5	"	334.9
			155.7	11.37	6,393.9	"	503.1
			217.5	10.53	7,893.9	"	671.0
			155.7	11.37	6,396.4	"	503.2
			99.81	11.97	4,480.5	"	335.0
			18.00	12.47	1,501.3	"	107.72
1905 May 24...	II	12.497	18.00	12.48	4,635.7	0.2884	107.09
			281.2	9.38	26,096	0.2876	797.8
			305.7	8.72	25,334	0.2875	832.1
			18.00	12.48	4,663.8	0.2884	107.58
May 25...	II	12.497	18.00	12.48	4,635.7	......	107.09
			281.2	9.38	26,104	......	798.4
			305.7	8.72	25,333	......	832.3
			18.00	12.48	4,651.8	......	107.30

TABLE 19.—*The conductivity data*—Continued.

SILVER NITRATE.

Date.	Cell No.	Concentration at 4°.	Temperature, t°.	Concentration at t°.	Conductance × 10^6.	Conductance capacity.	Equivalent conductance.
1904							
Jan. 27...	I	24.98	18.00	24.95	2,898	0.8974	104.22
			100.00	23.95	8,609	"	322.5
			154.9	22.78	12,200	"	480.4
			218.0	21.07	14,978	"	637.4
			155.3	22.78	12,221	"	481.1
			100.07	23.95	8,637	"	323.5
			18.00	24.95	2,928	"	105.22
Jan. 28 ..	I	24.98	18.00	24.95	2,893	......	104.03
			100.55	23.94	8,629	......	323.4
			156.2	22.75	12,247	......	483.0
			218.6	21.06	15,005	......	639.1
			156.5	22.74	12,283	......	484.5
			100.45	23.94	8,672	......	324.9
			18.00	24.95	2,917	......	104.83
Feb. 1..	I	24.98	18.00	24.95	2,893	......	104.04
			99.38	23.96	8,553	......	320.3
			154.8	22.78	12,168	......	479.1
			216.6	21.11	14,932	......	634.2
			155.1	22.77	12,189	......	480.1
			99.29	23.96	8,566	......	320.6
			18.00	24.95	2,905	......	104.43
Feb. 2...	I	24.98	18.00	24.95	2,895	......	104.12
			100.20	23.94	8,611	......	322.7
			156.4	22.75	12,250	......	483.2
			218.1	21.07	14,981	......	637.7
			156.6	22.73	12,321	......	486.1
			100.09	23.94	8,666	......	324.6
			18.00	24.95	2,923	......	105.06
Feb. 18 ..	I	24.98	18.00	24.95	2,892	......	104.01
			100.31	23.94	8,617	......	322.9
			156.4	22.74	12,254	......	483.3
			218.6	21.05	14,970	......	637.6
			156.2	22.75	12,245	......	482.8
			100.27	23.94	8,641	......	323.6
			18.00	24.95	2,906	......	104.44
			99.73	23.95	8,581	......	321.4
Feb. 23...	I	24.98	18.00	24.95	2,890	......	103.94
			155.4	22.77	12,231	......	481.9
			217.5	21.09	14,964	......	636.3
			155.4	22.77	12,236	......	482.0
			99.66	23.95	8,612	......	322.4
			18.00	24.95	2,908	......	104.51
Feb. 24...	I	24.98	18.00	24.95	2,893	......	104.04
			216.8	21.11	14,936	......	634.8
			18.00	24.95	2,918	......	104.86
Feb. 25...	I	24.98	18.00	24.95	2,892	......	103.99
			155.6	22.76	12,197	......	480.6
			18.00	24.95	2,900	......	104.23
April 15..	I	49.89	18.00	49.83	5,574.1	0.8958	100.19
			100.04	47.83	16,456	"	308.2
			156.3	45.42	23,242	"	458.2
			218.0	42.13	28,112	"	597.5
			155.7	45.45	23,227	"	457.6
			99.92	47.83	16,465	"	308.2
			18.00	49.83	5,584	"	100.33

TABLE 19.—*The conductivity data*—Continued.

Date.	Cell No.	Concentration at 4°.	Temperature, t°.	Concentration at t°.	Conductance × 10^6.	Conductance capacity.	Equivalent conductance.
			SILVER NITRATE.				
1905							
Nov. 16...	III	49.94	18.00	49.87	4,450.8	1.1252	100.42
Nov. 17...	III		18.00	49.87	4,452.6	1.1252	100.45
			305.0	35.23	21,912	1.1187	695.0
			280.2	37.80	23,179	1.1181	685.5
			18.00	49.87	4,455.9	1.1252	100.48
Nov. 18...	III	49.93	18.00	49.86	4,451.2	......	100.45
			280.9	37.68	23,156	......	687.1
			306.0	35.08	21,820	......	695.0
			18.00	49.86	4,440.1	......	100.16
1904							
Feb. 4...	I	99.92	18.00	99.79	10,519	0.8974	94.59
			100.21	95.77	30,915	"	289.7
			157.3	90.77	43,459	"	429.1
			218.1	84.56	51,677	"	548.3
			157.7	90.74	43,571	"	430.4
			100.15	95.77	30,927	"	289.7
			18.00	99.79	10,543	"	94.80
Feb. 5...	I	99.92	18.00	99.79	10,519	......	94.59
			100.14	95.77	30,894	......	289.4
			158.5	90.74	43,548	......	430.6
			218.1	84.56	51,680	......	548.4
			159.3	90.56	43,956	......	435.5
			100.15	95.77	30,949	......	289.9
			18.00	99.79	10,546	......	94.82
Feb. 25...	I	99.92	18.00	99.79	10,518	......	94.58
			155.8	91.02	43,236	......	426.3
			18.00	99.79	10,527	......	94.65
Apr. 16 ..	I	100.01	18.00	99.88	10,568	0.8958	94.77
			99.55	95.91	30,908	"	288.7
			155.4	91.14	43,322	"	425.7
			217.5	84.73	51,840	"	547.9
			155.4	91.14	43,358	"	426.1
			99.67	95.89	30,999	"	289.5
			18.00	99.88	10,583	"	94.90
1905							
Nov. 21 ..	III	99.85	18.00	99.72	8,433.8	1.1252	95.16
			281.0	75.71	(41,911)	1.1187	(619.0)
Nov. 23...	III		306.0	70.55	(39,154)	1.1181	(620.1)
			POTASSIUM SULPHATE.				
1904							
Mar. 14 ..	I	2.001	18.00	1.998	278.39	0.8967	124.58
			100.00	1.918	863.04	"	401.8
			155.9	1.822	1,236.0	"	605.6
			217.8	1.686	1,515.0	"	801.4
			155.8	1.823	1,240.7	"	606.7
			99.95	1.918	864.30	"	401.2
			18.00	1.998	280.08	"	124.63
Mar. 15 ..	I	1.999	18.00	1.996	277.72	......	124.41
			99.88	1.916	858.74	......	400.3
			155.7	1.821	1,236.8	......	606.2
			217.6	1.685	1,515.0	......	801.3
			155.6	1.821	1,237.0	......	605.2
			99.81	1.916	859.27	......	399.4
			18.00	1.996	278.50	......	124.07

TABLE 19.—*The conductivity data*—Continued.

POTASSIUM SULPHATE—Continued.

Date.	Cell No.	Concentration at 4°.	Temperature, t°.	Concentration at t°.	Conductance $\times 10^6$.	Conductance capacity.	Equivalent conductance.
1905							
Apr. 3 ..	II	2.001	18.00	1.999	845.9	0.2974	125.42
			277.2	1.516	4,727.3	0.2966	916.0
			305.4	1.399	4,417.8	0.2965	933.7
			18.00	1.999	849.9	0.2974	125.22
Apr. 4 ..	II	2.001	18.00	1.999	842.6	......	124.94
			277.2	1.515	4,748.8	......	920.5
			305.4	1.398	4,426.3	......	929.1
			18.00	1.999	847.7	......	125.00
Apr. 21 ..	II	1.999	18.00	1.996	847.0	0.2950	124.76
			280.5	1.502	4,780.5	0.2942	927.2
			305.0	1.398	4,470.1	0.2941	930.5
			18.00	1.996	853.2	0.2950	124.87
July 12 ..	II	2.001	18.00	1.998	859.7	0.2913	125.03
			281.1	1.502	4,858.6	0.2905	930.7
			305.6	1.397	4,471.3	0.2904	919.4
			18.00	1.998	895.6	0.2913	129.33
July 13...	II	2.003	18.00	2.000	857.6	......	124.44
			281.0	1.504	4,852.2	......	928.3
			305.5	1.397	4,480.9	......	920.2
			18.00	2.000	880.3	......	126.98
Mar. 16 ..	I	12.505	18.00	12.490	1,588.5	0.8967	114.00
			99.86	11.989	4,815.8	"	359.9
			156.1	11.388	6,755.4	"	531.5
			217.8	10.547	7,880.8	"	669.2
			156.2	11.387	6,761.8	"	531.9
			99.88	11.989	4,819.5	"	360.0
			18.00	12.490	1,591.6	"	114.10
Mar. 17 ..	I	12.508	18.00	12.490	1,590.5	......	114.13
			100.38	11.985	4,844.3	......	362.2
			156.7	11.381	6,782.9	......	534.0
			218.4	10.542	7,895.8	......	671.0
			156.7	11.381	6,788.9	......	534.3
			100.30	11.985	4,845.2	......	362.1
			18.00	12.490	1,592.6	......	114.17
1905							
Apr. 6 ..	II	12.503	18.00	12.487	4,799.6	0.2972	114.14
Apr. 10 ..	II	12.493	18.00	12.477	4,800.3	0.2965	114.02
			275.5	9.507	22,460	0.2954	696.2
			304.9	8.753	19,463	0.2953	655.0
			18.00	12.477	4,811.9	0.2962	114.03
Apr. 12 ..	II	12.492	18.00	12.476	4,807.7	0.2962	114.07
			275.6	9.503	22,528	0.2951	698.0
			305.1	8.746	19,496	0.2950	656.0
			280.6	9.394	22,292	0.2951	698.6
			18.00	12.476	4,818.8	0.2959	114.08
Apr. 13 ..	II	12.490	18.00	12.473	4,813.0	0.2959	114.10
			280.7	9.392	22,281	0.2948	697.7
			305.2	8.744	19,523	0.2947	656.4
			18.00	12.473	4,817.5	0.2956	113.97
May 1 ..	II	12.497	18.00	12.481	4,841.0	0.2951	114.37
			281.2	9.388	22,214	0.2940	694.0
			305.3	8.748	19,531	0.2939	654.4
			18.00	12.481	4,845.5	0.2948	114.25

TABLE 19.—*The conductivity data*—Continued.

Date.	Cell No.	Concentration at 4°.	Temperature, t°.	Concentration at t°.	Conductance $\times 10^6$.	Conductance capacity.	Equivalent conductance.
BARIUM NITRATE—Continued.							
1904							
Oct. 4 ..	III	50.17	18.00	50.11	3,827.7	1.1372	86.85
Oct. 5 ..	III		18.00	50.11	3,836.0	1.1359	86.94
			280.8	37.86	17,191	1.1284	512.0
Oct. 12 ..	III	50.19	18.00	50.12	3,845.9	1.1349	87.08
			281.2	37.86	17,086	1.1272	508.6
			305.5	35.29	14,597	1.1266	465.5
			18.00	50.12	3,817.9	1.1337	86.29
Oct. 22 ..	III	50.09	18.00	50.02	3,860.1	1.1274	86.97
			305.5	35.22	14,703	1.1190	466.7
			18.00	50.02	3,885.6	1.1261	87.41
Oct. 20 ..	III	78.72	18.00	78.62	5,696.4	1.1320	82.03
			281.0	59.53	24,606	1.1247	465.6
			305.1	55.60	21,025	1.1241	424.7
			18.00	78.62	5,670.2	1.1312	81.56
Oct. 25 ..	III	78.73	18.00	78.63	5,726.4	1.1261	82.02
			281.2	59.51	24,742	1.1187	464.8
			305.7	55.52	21,120	1.1181	425.2
			18.00	78.63	5,705.9	1.1252	81.63
Apr. 12 ..	I	100.07	18.00	99.95	8,830.1	0.8960	79.14
			99.50	95.97	26,789	"	250.1
			155.3	91.22	37,027	"	363.6
			217.3	84.83	42,075	"	444.7
			18.00	99.95	8,832.4	"	79.14
Apr. 13 ..	I	100.00	18.00	99.87	8,819.1	......	79.11
			99.80	95.87	26,850	......	250.9
			155.5	91.07	37,079	......	364.5
			217.5	84.68	42,012	......	444.8
			155.5	91.07	37,179	......	364.5
			99.77	95.88	26,846	......	250.8
			18.00	99.87	8,821.4	......	79.11
1905							
Oct. 14 ..	III	100.34	18.00	100.21	6,995.4	1.1337	79.14
			281.3	75.97	29,526	1.1263	437.3
			18.00	100.21	6,693.0	1.1328	75.60
Oct. 17 ..	III	100.40	18.00	100.28	7,004.0	1.1328	79.12
			280.9	76.12	29,763	1.1255	439.8
			18.00	100.28	7,019.0	1.1320	79.21
MAGNESIUM SULPHATE.							
1904							
June 28 ..	II	1.982	18.00	1.979	611.07	0.3070	94.43
			100.07	1.900	1,894.2	0.3068	304.4
			155.7	1.805	2,280.7	0.3066	384.7
			217.7	1.670	1,537.5	0.3064	277.6
			155.9	1.805	2,290.4	0.3066	385.6
			100.05	1.900	1,907.3	0.3068	305.7
			18.00	1.979	614.67	0.3070	94.55
June 28 ..	II	2.168	18.00	2.165	661.16	......	93.41
			100.12	2.078	2,045.2	......	300.5
			155.9	1.975	2,440.7	......	376.4
			217.8	1.827	1,628.8	......	269.1
			155.9	1.975	2,457.6	......	378.3
			100.12	2.078	2,056.6	......	301.4
			18.00	2.165	665.82	......	93.68

TABLE 19.—*The conductivity data*—Continued.

MAGNESIUM SULPHATE—Continued.

Date.	Cell No.	Concentration at 4°.	Temperature, t°.	Concentration at t°.	Conductance × 10^6.	Conductance capacity.	Equivalent conductance.
1904							
May 6 ..	I	12.529	18.00	12.51	1,032.6	0.8954	73.83
			100.14	12.01	2,877.8	"	214.4
			156.7	11.41	2,951.7	"	231.4
			219.3	10.55	1,629.3	"	137.7
			156.7	11.41	2,953.4	"	231.4
			100.11	12.01	2,881.0	"	214.4
			18.00	12.51	1,035.3	"	73.91
Apr. 25 ..	I	26.16	18.00	26.13	1,880.9	......	64.41
			99.55	25.09	5,026.7	......	179.2
			155.7	23.84	4,961.8	......	186.2
			217.8	22.09	2,678.7	......	108.3
			155.6	23.84	4,964.7	......	186.2
			99.49	25.09	5,026.9	......	179.3
			18.00	26.13	1,882.9	......	64.44
Apr. 26 ..	I	52.83	18.00	52.76	3,324.2	......	56.40
			99.70	50.65	8,581.5	......	151.7
			155.8	48.13	8,186.0	......	152.2
			218.0	44.62	4,342.7	......	87.0
			155.8	48.13	8,190.7	......	152.3
			99.84	50.65	8,590.4	......	151.8
			18.00	52.76	3,332.8	......	56.52
Apr. 28 ..	I	99.93	~ 18.00	99.81	5,552.4	......	49.81
			100.07	95.79	14,017	......	131.0
			156.5	90.98	13,088	......	128.8
			218.6	84.62	7,015.0	......	74.1
			18.00	99.81	5,568.5	......	49.92
Apr. 28 ..	I	99.93	18.00	99.81	5,552.4	......	49.81
			156.4	90.99	13,109	......	129.0
			18.00	99.81	5,555.0	......	49.82
Apr. 27 ..	I	106.83	18.00	106.69	5,851.1	......	49.10
			100.05	102.40	14,739	......	128.9
			156.5	97.26	13,754	......	126.6
			218.6	90.42	7,340.5	......	72.6
			156.5	97.26	13,766	......	126.7
			100.03	102.40	14,766	......	129.1
			18.00	106.69	5,869.2	......	49.23
May 2 ..	I	195.96	18.00	195.71	9,467.9	......	43.31
			100.09	187.83	23,561	......	112.3
			156.7	178.36	21,896	......	109.9
			218.8	166.49	11,384	......	61.2
			156.3	178.44	21,955	......	110.3
			100.11	187.82	23,619	......	112.5
			18.00	195.71	9,485.9	......	43.40
May 3 ..	I	350.9	18.00	350.4	15,044	......	38.44
			100.31	336.2	37,372	......	99.53
			156.5	319.4	35,115	......	98.46
			218.8	......	......	......	......
			156.6	319.4	35,115	......	98.46
			18.00	350.4	15,075	......	38.51

In regard to these experiments a few remarks of a special character may be added. In the case of silver nitrate it was observed, when the bomb was rinsed with absolute alcohol and ether and the adhering portion of the latter solvent allowed to evaporate, that there was, even at 218°, a rapid progressive decrease in the conductance of the solution and that this was due to an extensive reduction of the salt. In fact, in two experiments, one at 218° and one at 306°, it was found upon cooling and opening the bomb that it was entirely coated with a crystalline deposit of metallic silver, and that the solution contained no silver and no acid whatever, giving no precipitate with hydrochloric acid and no color change with litmus. Since the minute quantity of organic matter present could not possibly cause this reduction, it is evident that the decomposition *when once started* goes on spontaneously, the reaction being apparently catalyzed by the metallic silver. This remarkable phenomenon was not observed when the bomb was rinsed with pure water and quickly dried at 100°, or when rinsed with the solution, except in the last experiments at 281° and 306° made with the strongest (100 milli-normal) solution; in these cases a slow decrease in conductance occurred, and the conductivity-values given are therefore less reliable than usual; yet since they have been corrected upon the basis of measurements of the rate of change they are probably not in error by more than 1 per cent.

In the case of the 100 milli-normal barium nitrate solution at 306° a steady decrease in conductance was also observed, but, since upon returning to 18° the conductance was found to be the same as before the heating, the observed change was doubtless due to the gradual separation of the salt itself or of a basic derivative of it from the solution. We did not therefore obtain reliable measurements at this concentration at 306°, but in place of them we investigated at that temperature a somewhat more dilute solution (80 milli-normal) in which the change, though noticeable, was so slow as to introduce no important error.

In the experiments with magnesium sulphate a similar decrease in conductance was observed with the 350 milli-normal solution at 218° and even with an 80 milli-normal solution at 306°. In the former case a white crystalline deposit was found in the bomb upon cooling and opening it without shaking, and the solution was found by titration to contain considerable acid. On account of the large hydrolysis and the separation of a solid phase, even in fairly dilute solution, no attempt was made to carry the measurements above 218°.

40. SUMMARY OF THE EQUIVALENT-CONDUCTANCE VALUES.

The separate conductance values given in table 19 were all corrected so as to correspond to the uniform temperatures of 18°, 100°, 156°, 218°, 281°, and 306° by means of temperature-coefficients obtained by plotting those values. The so-corrected equivalent conductances are summarized in table 20. The concentration is expressed in milli-equivalents per liter at 4°. In the columns headed "Initial" are given the equivalent conductances obtained from the measurement at the temperature in question before going to the higher temperatures; while in the columns headed "Final" are given the equivalent conductances obtained after returning to the temperature in question from the higher ones. From a comparison of the separate initial values at any temperature and concentration the degree of agreement of determinations made at different times, and often with different solutions, will be seen. A comparison of the initial and final values in the separate experiments shows the contamination that resulted from the heating.

TABLE 20.—*Equivalent conductance at round temperatures.*

SODIUM CHLORIDE.

Date.	Concentration at 4°.	18°.		100°.	218°.	281°.	306°.
		Initial.	Final.				
1905							
Mar. 25 ..	2.000	105.71	106.22	......	......	......	972
Nov. 13 ..	2.006	105.5	105.5	349.3	......	......	......
1904							
Mar. 31 ..	10.013	102.02	102.01	......	691.3	......	......
July 1 ..	10.020	101.96	102.12	......	688.4	......	......
Mean ..	10.017	101.99	102.07	......	689.9	......	......
1905							
Mar. 15 ..	10.027	101.91	101.89	......	......	830.0	879.8
Mar. 17 ..	10.009	101.96	102.86	......	......	836.7	886.8
Mar. 21 ..	10.021	101.93	103.07	......	......	835.1	884.0
Mar. 23 ..	10.015	101.94	102.14	......	......	835.2	883.4
Mar. 29 ..	9.974	102.02	102.07	......	......	836.3	885.4
Apr. 23 ..	10.017	101.94	101.98	......	......	837.2	887.2
Mean ..	10.010	101.95	102.33	......	......	835.1	884.5
1904							
Apr. 1 ..	100.13	92.14	92.18	......	588.0	......	......
1905							
Sept. 26 ..	100.13	92.08	92.22	......	......	678.7	694.4
Oct. 1 ..	100.17	92.08	92.34	......	......	678.7	693.5
Mean ..	100.15	92.08	92.28	......	......	678.7	694.0
Nov. 28 ..	100.02	91.94	92.01	296.8	156° 445.5	......	......

TABLE 20.—*Equivalent conductance at round temperatures*—Continued.

POTASSIUM CHLORIDE.

Date.	Concentration at 4°.	18°.		218°.	281°.	306°.
		Initial.	Final.			
1904						
Mar. 25..	10.015	122.38	122.68	746.8	......	......
1905						
Mar. 13..	10.021	122.40	......	......	......	935.4
Mar. 14..	10.021	122.40	122.41	......	889.8	......
Apr. 24..	10.008	122.45	122.51	......	887.6	935.6
Mean .	10.016	122.42	122.46	......	888.7	935.5
1904						
Mar. 28..	100.13	111.98	112.18	637.7	......	......
1905						
Sept. 27..	100.12	111.97	......	......	......	......
Oct. 2..	100.20	111.97	112.20	......	724.5	736.2
Oct. 9..	100.17	112.03	......	......	......	......
Oct. 27..	100.04	112.03	112.35	......	729.4	......
Mean .	100.13	112.00	112.27	......	727.0	736.2

Date.	Concentration at 4°.	18°.		25°.	50°.	75°.	100°.	128°.	140°.	156°.
		Initial.	Final.							
1905										
Nov. 18..	2.002	126.4	126.2	146.4	......	......	393.3	......	534.2	589.1
Nov. 21..	9.996	122.4	122.5	141.5	215.3	295.4	377.7	471.8	......	563.0
Nov. 20..	19.992	120.1	120.1	138.8	210.4	......	368.3	......	......	......
Nov. 25..	100.01	112.0	112.0	129.0	194.7	265.1	336.7	417.1	449.7	492.8

TABLE 20.—*Equivalent conductance at round temperatures*—Continued.

SILVER NITRATE.

Date.	Concentration at 4°.	18°.		100°.		156°.		218°.	281°.	306°.
		Initial.	Final.	Initial.	Final.	Initial.	Final.			
1904										
Feb. 16.....	1.999	112.02	113.35	351.7	353.5	533.0	536.3	722.0	......	......
Feb. 17.....	1.999	112.14	112.89	352.1	353.9	533.9	534.7	720.6	......	......
June 27.....	2.002	112.25	113.18	350.7	353.3	534.0	536.0	729.6	......	......
Mean	2.000	112.14	113.14	351.5	353.6	533.6	535.7	724.1	......	......
1905										
May 19.....	2.003	112.62	117.31	.....	.....	.....	.....	.....	896.1	957.0
May 22.....	1.999	112.38	115.75	.....	.....	.....	.....	.....	895.3	953.7
May 23.....	2.002	112.10	115.30	.....	.....	.....	.....	.....	892.8	952.7
July 11.....	2.004	112.32	118.20	.....	.....	.....	.....	.....	......	956.8
Mean	2.002	112.29	116.64	.....	.....	.....	.....	.....	894.7	955.1
1904										
April 14.....	12.481	107.55	107.72	335.3	335.5	504.0	504.1	672.2	......	......
1905										
May 24.....	12.497	107.09	107.58	.....	.....	.....	.....	.....	797.6	831.9
May 25.....	12.497	107.09	107.30	.....	.....	.....	.....	.....	798.2	832.1
Mean	12.497	107.09	107.44	.....	.....	.....	.....	.....	797.9	832.0
1904										
Jan. 27.....	24.98	104.22	105.22	322.5	323.2	483.4	482.8	637.4	......	......
Jan. 28.....	24.98	104.03	104.83	321.8	323.6	482.5	483.0	638.0	......	......
Feb. 1.....	24.98	104.04	104.43	322.1	322.7	482.3	482.5	637.0	......	......
Feb. 2.....	24.98	104.12	105.06	322.2	324.3	482.1	484.5	637.5	......	......
Feb. 18.....	24.98	104.01	104.44	322.0	322.8	482.2	482.3	636.5	......	......
Feb. 23.....	24.98	103.94	104.51	322.2	323.4	483.5	483.6	637.3	......	......
Feb. 24.....	24.98	104.04	104.86	.....	.....	.....	.....	636.8	......	......
Feb. 25.....	24.98	103.99	104.23	.....	.....	.....	481.7	.....	......	......
Mean	24.98	104.05	104.70	322.1	323.3	482.5	483.1	637.2	......	......
1904										
Apr. 15.....	49.89	100.19	100.33	308.1	308.4	457.4	458.4	597.5	......	......
1905										
Nov. 16.....	49.94	100.42	......	.....	.....	.....	.....	.....	......	......
Nov. 17.....	49.94	100.45	100.48	.....	.....	.....	.....	.....	685.5	694.5
Nov. 18.....	49.93	100.45	100.16	.....	.....	.....	.....	.....	687.1	695.0
Mean	49.94	100.44	......	.....	.....	.....	.....	.....	686.3	694.8
1904										
Feb. 4.....	99.92	94.59	94.80	289.3	289.4	425.9	426.2	548.1	......	......
Feb. 5.....	99.92	94.59	94.82	289.1	289.6	424.4	427.1	548.2	......	......
Feb. 25.....	99.92	94.58	94.65	.....	.....	426.8	.....	.....	......	......
April 16.....	100.01	94.77	94.90	289.6	290.1	427.2	427.6	548.9	......	......
Mean	99.94	94.64	94.79	289.3	289.7	426.1	427.0	548.4	......	......
Nov. 21.....	99.85	95.16	......	.....	.....	.....	.....	.....	(619.)	......
Nov. 23.....	......	......	......	.....	.....	.....	.....	.....	......	(620.)

TABLE 20.—*Equivalent conductance at round temperatures*—Continued.

Date.	Concentration at 4°.	18°.		100°.		156°.		218°.	281°.	306°.
		Initial.	Final.	Initial.	Final.	Initial.	Final.			
POTASSIUM SULPHATE.										
1904										
Mar. 14.....	2.001	124.58	124.63	401.8	401.4	606.0	607.4	802.0	......	......
Mar. 15.....	1.999	124.41	124.07	400.7	400.1	607.2	606.6	802.4	......	......
Mean	2.000	124.50	124.35	401.3	400.8	606.6	607.0	802.2	......	......
1905										
April 3.....	2.001	125.42	125.22	.....	.....	.....	.....	.....	919.8	933.3
April 4.....	2.001	124.94	125.00	.....	.....	.....	.....	.....	924.3	928.7
April 21.....	1.999	124.76	124.87	.....	.....	.....	.....	.....	927.7	929.9
July 12.....	2.001	125.03	129.33	.....	.....	.....	.....	.....	930.6	919.2
July 12.....	2.003	124.44	126.98	.....	.....	.....	.....	.....	928.3	919.9
Mean	2.001	124.92	126.28	.....	.....	.....	.....	.....	926.1	926.2
1904										
Mar. 16.....	12.503	114.00	114.10	360.3	360.4	531.2	531.3	669.5	......	......
Mar. 17.....	12.508	114.13	114.17	361.0	361.1	532.0	532.3	670.4	......	......
Mean	12.506	114.07	114.14	360.7	360.8	531.6	531.8	670.0	......	......
1905										
April 6.....	12.503	114.13	......	.....	.....	.....	.....	.....	......	......
April 10.....	12.493	114.02	114.03	.....	.....	.....	.....	.....	696.2	652.8
April 12.....	12.492	114.07	114.08	.....	.....	.....	.....	.....	698.0	654.2
April 13.....	12.490	114.10	113.97	.....	.....	.....	.....	.....	697.7	654.6
May 1.....	12.497	114.37	114.25	.....	.....	.....	.....	.....	694.0	653.0
Mean	12.495	114.14	114.08	.....	.....	.....	.....	.....	696.5	653.7
1904										
Mar. 18.....	50.05	102.03	102.14	313.7	313.5	449.0	448.9	537.9	......	......
Mar. 21.....	50.00	102.05	102.11	313.9	313.9	450.1	450.4	538.6	......	......
Mean	50.03	102.04	102.13	313.8	313.7	449.6	449.7	538.3	......	......
1905										
Sept. 29.....	50.12	102.02	102.33	.....	.....	.....	.....	.....	527.3	481.6
Sept. 29.....	50.04	102.06	102.31	.....	.....	.....	.....	.....	526.4	480.3
Mean	50.08	102.04	102.32	.....	.....	.....	.....	.....	526.8	481.0
1904										
Mar. 22.....	100.13	95.05	95.04	288.0	287.9	407.3	407.3	477.0	......	......
Mar. 23.....	100.16	95.06	95.05	288.0	288.1	407.4	407.5	477.6	......	......
Mean	100.15	95.06	95.05	288.0	288.0	407.4	407.4	477.3	......	......
1905										
Sept. 30.....	100.03	94.97	95.01	.....	.....	.....	.....	.....	455.1	410.5
Sept. 30.....	100.07	94.86	94.88	.....	.....	.....	.....	.....	454.1	409.6
Mean	100.05	94.92	94.94	.....	.....	.....	.....	.....	454.6	410.0
BARIUM NITRATE.										
1904										
April 7.....	1.999	109.52	109.05	352.5	351.1	540.1	538.2	720.7	......	......
April 8.....	1.999	109.55	109.26	352.7	352.2	538.2	538.2	724.2	......	......
Mean	1.999	109.54	109.16	352.6	351.7	539.2	538.2	722.5	......	......
1905										
May 2.....	1.997	110.08	110.51	.....	.....	.....	.....	.....	863.8	877.0
May 3.....	2.003	109.83	110.00	.....	.....	.....	.....	.....	863.8	880.1
Mean	2.000	109.95	110.26	.....	.....	.....	.....	.....	863.8	878.6
1904										
April 11.....	12.512	99.48	99.47	317.4	317.5	476.1	475.7	614.9	......	......

TABLE 20.—*Equivalent conductance at round temperatures*—Continued.

BARIUM NITRATE.

Date.	Concentration at 4°.	18°.		100°.		156°.		218°.	281°.	306°.
		Initial.	Final.	Initial.	Final.	Initial.	Final.			
1905										
May 4.....	12.512	99.48	......	.....	.....	.....	.....	.....	......	......
May 5.....	12.508	99.51	100.23	.....	.....	.....	.....	.....	665.6	633.2
May 8.....	12.496	99.48	99.73	.....	.....	.....	.....	.....	664.7	631.7
Mean	12.504	99.49	99.98	.....	.....	.....	.....	.....	665.1	632.5
1904										
April 12.....	50.05	86.97	87.02	275.5	275.6	404.6	404.6	502.9	......	......
1905										
Oct. 2.....	50.09	86.95	......	.....	.....	.....	.....	.....	507.2	462.2
Oct. 3.....	50.16	86.93	......	.....	.....	.....	.....	.....	......	......
Oct. 3.....	"	87.00	......	.....	.....	.....	.....	.....	......	......
Oct. 4.....	50.17	86.85	......	.....	.....	.....	.....	.....	......	......
Oct. 5.....	"	86.94	......	.....	.....	.....	.....	.....	511.8	......
Oct. 12.....	50.19	87.08	86.29	.....	.....	.....	.....	.....	508.8	464.5
Oct. 22.....	50.09	86.97	87.41	.....	.....	.....	.....	.....	......	465.7
Mean	......	86.96	......	.....	.....	.....	.....	.....	509.3	464.1
Oct. 20.....	78.72	82.03	81.56	.....	.....	.....	.....	.....	465.6	422.9
Oct. 25.....	78.73	82.02	81.63	.....	.....	.....	.....	.....	465.0	424.6
Mean	78.73	82.03	......	.....	.....	.....	.....	.....	465.3	423.8
1904										
April 12.....	100.07	79.14	79.14	251.2	.....	364.8	.....	445.1	......	......
April 13.....	100.00	79.11	79.11	251.3	251.3	365.4	365.4	445.1	......	......
Mean	100.04	79.13	79.13	251.3	251.3	365.1	365.4	445.1	......	......
1905										
Oct. 14.....	100.34	79.14	75.60	.....	.....	.....	.....	.....	437.6	......
Oct. 17.....	100.40	79.12	79.21	.....	.....	.....	.....	.....	439.6	......
Mean	100.37	79.13	......	.....	.....	.....	.....	.....	438.6	......

MAGNESIUM SULPHATE.

Date.	Concentration at 4°.	18°.		100°.		156°.		218°.
		Initial.	Final.	Initial.	Final.	Initial.	Final.	
1904								
June 28	1.982	94.43	94.56	304.3	305.6	384.7	385.6	276.5
June 28	2.168	93.41	93.68	300.3	301.2	376.4	378.3	268.4
Corrected values....	2.000	94.3	.....	304.0	.....	384.0	.....	275.7
May 6.......	12.529	73.83	73.91	214.2	214.3	231.4	231.4	140.0
Corrected values....	12.500	73.9	.....	214.3	.....	231.5	.....	140.1
Apr. 25.......	26.16	64.41	64.44	179.6	179.7	185.9	185.9	107.4
Corrected values....	25.00	64.8	.....	180.7	.....	187.0	.....	108.0
Apr. 26.......	52.83	56.40	56.52	151.9	151.9	151.9	152.0	86.5
Corrected values....	50.00	56.8	.....	153.1	.....	153.1	.....	87.1
Apr. 28.......	99.93	49.81	49.92	131.0	.....	129.0	.....	74.4
Apr. 28.......	99.93	49.81	49.82	.....	.....	129.1	.....	.....
Apr. 27.......	106.83	49.10	48.23	128.9	129.1	126.8	126.9	72.9
Corrected values....	100.00	49.8	.....	131.0	.....	129.0	.....	74.4
May 2.......	195.96	43.31	43.40	112.3	112.4	110.2	110.3	61.6
May 3.......	350.9	38.44	38.51	99.7	.....	98.7	98.7	.....

Table 21 contains a summary of best values derived from the means in table 20. The means of only the initial values have been taken and these have been corrected for the contamination upon heating in the manner described in section 16, Part II.

TABLE 21.—*Best values of the equivalent conductance at round temperatures.*

Temperature ($t°$)	Sodium chloride.		Potassium chloride.		Silver nitrate.	
	Concentration at $t°$.	Equivalent conductance.	Concentration at $t°$.	Equivalent conductance.	Concentration at $t°$.	Equivalent conductance.
18	2.000	105.6	2.000	126.4	1.998	112.2
	10.00	102.0	10.00	122.4	12.48	107.2
	100.0	92.0	100.0	112.0	24.95	104.0
					49.86	100.2
					99.8	94.6
100	1.924	349.3	1.920	393.3	1.916	351.0
	95.9	296.8	9.58	377.7	11.97	335.0
			95.9	336.7	23.95	321.5
					47.83	308.0
					95.8	289.0
156	91.1	445.5	1.824	589	1.821	532
			9.10	563	11.37	504
			91.1	493	22.75	481.0
					45.43	457.0
					91.0	426.0
218	8.44	690	8.44	746	1.685	720
	84.4	588	84.4	637	10.52	672
					21.07	635
					42.13	597
					84.6	548
281	7.53	834	7.51	889	1.500	877
	75.7	678	75.6	726	9.38	796
					37.70	685
					75.7	(616)
306	1.394	972	6.99	935	1.394	937
	6.99	883	70.5	735	8.71	830
	70.5	694			35.10	693
					70.6	(617)

TABLE 21.—***Best values of equivalent conductance at round temperatures***—Continued.

Temperature (t°)	Potassium chloride.		Temperature (t°)	Potassium chloride.	
	Concentration at t°.	Equivalent conductance.		Concentration at t°.	Equivalent conductance.
25	1.997	146.4	75°	9.75	295.4
	9.97	141.5		97.5	265.1
	19.93	138.8			
	99.7	129.0			
50	9.88	215.3	128°	9.36	471.8
	19.76	210.4		93.6	417.1
	98.8	194.7			

Temperature (t°)	Potassium sulphate.		Barium nitrate.		Magnesium sulphate.	
	Concentration at t°.	Equivalent conductance.	Concentration at t°.	Equivalent conductance.	Concentration at t°.	Equivalent conductance.
18	1.998	124.8	1.996	109.7	1.998	94.3
	12.48	114.1	12.51	99.5	12.49	73.9
	50.00	102.0	50.07	87.0	24.98	64.8
	100.0	95.0	78.6	82.0	49.95	56.8
			100.1	79.1	99.9	49.8
					195.7	43.3
					350.4	38.45
100	1.918	401.5	1.916	353.0	1.919	304.0
	11.99	360.5	12.01	317.5	11.99	214.3
	47.95	313.5	47.98	275.5	23.98	180.7
	96.0	288.0	95.9	251.0	47.97	153.1
					95.9	131.0
					187.8	112.3
					336.3	99.7
156	1.821	607	1.821	539	1.822	384.0
	11.39	532	11.41	476.0	11.39	231.5
	45.56	449.5	45.58	404.5	22.77	187.0
	91.2	407.5	91.1	365.5	45.55	153.1
					91.1	129.0
					178.5	110.2
					319.5	98.7
218	1.685	802	1.685	723	1.685	275.7
	10.55	670	10.55	615	10.53	140.1
	42.27	538	42.24	503	21.07	108.0
	84.8	477.5	84.7	445.0	42.13	87.1
					84.3	74.4
					166.7	61.6
281	1.503	920	1.501	862	......	......
	9.39	697	9.43	664	......	......
	37.71	526	37.85	509	......	......
	75.6	454.5	59.5	465.5	......	......
			76.0	438.5	......	......
306	1.395	920	1.392	877	......	......
	8.73	654	8.77	631	......	......
	35.07	480.5	35.19	464	......	......
	70.36	410.0	55.5	424	......	......

41. EQUIVALENT-CONDUCTANCE VALUES AT ROUND CONCENTRATIONS.

The conductance values in table 21 which refer to different concentrations at different temperatures have been reduced to a uniform round concentration by graphic interpolation with the help of the linear function $\frac{1}{\Lambda}=\frac{1}{\Lambda_0}+K(C\Lambda)^m$ discussed in section 17. The so-reduced values are presented in table 22, except those for sodium and potassium chlorides, which have already been summarized in table 9, section 16. As these are our final values it may be again stated in explanation of the table, that, as in the preceding tables, the concentration is expressed in milli-equivalents per liter based on the international atomic weights for 1905 referred to oxygen as 16.00; that the temperature is the true temperature on the hydrogen-gas scale as derived (at the higher temperatures) from the determinations of Jaquerod and Wassmer of the boiling-points of naphthalene and benzophenone; and that the equivalent conductance, which has been corrected for that of the water, is expressed in reciprocal ohms, the absolute conductance-capacity of the conductivity vessel having been derived from Kohlrausch and Maltby's data for sodium and potassium chloride at 18° and corrected for its change with the temperature. The concentration given in the second column is that at the temperature of the measurement.

The conductances at zero concentration were obtained in the cases of silver nitrate, barium nitrate, and potassium sulphate, at 100° and above, by graphic extrapolation upon plots of the function $\frac{1}{\Lambda}=\frac{1}{\Lambda_0}+K(C\Lambda)^m$ At the higher temperatures the results are doubtless much in error owing to the large extrapolation involved, but they are the best obtainable from the data. At 18° we have inserted for zero concentration the values calculated from Kohlrausch's conductance values for the separate ions of the potassium sulphate, barium nitrate, and magnesium sulphate. In the case of magnesium sulphate at the higher temperatures, the method employed for the other salts was inapplicable owing to the large hydrolysis, and there are at present no independent data upon which a fully satisfactory determination of its Λ_0 value can be based. But, in order to give some idea of the relation of its conductivity at the various concentrations to that of the completely ionized salt, we have assumed that, at 100° and above, magnesium and barium ions have the same equivalent conductance and have computed rough Λ_0 values by the relation $\Lambda_{0(MgSO_4)}=\Lambda_{0(BaN_2O_6)}+\Lambda_{0(K_2SO_4)}-\Lambda_{0(KCl)}$. The assumption that chloride-ion and nitrate-ion have the same equivalent conductance is also involved; but this assumption is doubtless substantially correct. The so-computed Λ_0 values for magnesium sulphate are given within parentheses in the table.

TABLE 22.—*Final values of the equivalent conductance.*

Substance.	Concentration.	18°.	100°.	156°.	218°.	281°.	306°.
$AgNO_3$	0	115.8	367	570	780	965	1065
	2.0	112.2	353	539	727	877	935
	10.0	108.0	337	507	673	790	818
	12.5	107.2	334.5	......	......	......	......
	20.0	105.1	325.5	487.5	639	......	......
	25.0	104.0	322.5	......	......	......	......
	40.0	101.3	311.5	462.0	599	680	680
	50.0	99.9	307.5	......	......	......	......
	80.0	96.5	294.0	432.0	552	614	604
	100.0	94.6	289.0	......	......	......	......
K_2SO_4	0	132.8	455	715	1065	1460	1725
	2.0	124.8	401.5	605	806	893	867
	10.0	115.7	365.0	537	672	687	637
	12.5	114.1	358.0	......	......	......	......
	40.0	104.2	320.0	455.0	545	519	466.0
	50.0	102.0	312.0	......	......	......	......
	80.0	97.2	294.5	415.0	482.0	448.0	395.5
	100.0	95.0	286.0	......	......	......	......
$Ba(NO_3)_2$.	0	116.9	385	600	840	1120	1300
	2.0	109.7	352.0	536	715	828	824
	10.0	101.0	322.0	481	618	658	615
	12.5	99.4	316.0	......	......	......	......
	40.0	88.7	280.0	412	507	503	448
	50.0	86.8	273.5	......	......	......	......
	80.0	81.6	257.5	372	449	430	......
	100.0	79.1	249.0	......	......	......	......
$MgSO_4$	0	114.1	(426)	(690)	(1080)	......	......
	2.0	94.3	302	377	260	......	......
	10.0	76.1	223.5	241.0	143	......	......
	12.5	73.9	212.5	225.0	......	......	......
	20.0	67.5	190.0	195.0	110.5	......	......
	25.0	64.8	179.0	180.0	......	......	......
	40.0	59.3	160.0	158.0	88.5	......	......
	50.0	56.8	151.5	149.0	......	......	......
	80.0	52.0	136.0	133.0	75.2	......	......
	100.0	49.8	129.5	126.0	......	......	......
	160.0	45.3	116.5	114.8	62.4	......	......
	200.0	43.1	110.5	109.1	......	......	......
	320.0	39.2	100.6	98.7	......	......	......

It is of interest to compare our results at 18° with those previously obtained by Kohlrausch and Steinwehr*, Kohlrausch and Grüneisen,† and (for magnesium sulphate) by Foster.‡ All these data at corresponding concentrations have been brought together in table 23. It will be seen that the results agree within 0.2 per cent in nearly all cases, and within 0.4 per cent without exception. Measurements have been made at 95° in a glass apparatus by Kahlenberg§ with silver nitrate and magnesium sulphate.

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*Kohlrausch und Steinwehr, Sitzungsber. preuss. Akad., 1902, 581.
†Kohlrausch und Grüneisen, Sitzungsber. preuss. Akad., 1904, 1215.
‡W. Foster, Phys. Rev., 8, 257 (1899).
§Kahlenberg, J. Phys. Chem., 5, 349 (1901).

We have reduced his results to 100° by means of our temperature-coefficients at that temperature, and have given them beside our own in the table. It will be seen that the results with silver nitrate are widely divergent at all concentrations, and that those with magnesium sulphate are somewhat so except at the higher concentrations, indicating the difficulty of getting reliable results at such high temperatures in glass vessels.

TABLE 23.—*Comparison of the conductivity results of different investigators.*

Temperature.	Concentration.	Silver nitrate.		Barium nitrate.		Potassium sulphate.		Magnesium sulphate.		
		Noyes and Melcher.	Kohlrausch and Steinwehr.*	Noyes and Melcher.	Kohlrausch and Grüneisen.†	Noyes and Melcher.	Kohlrausch and Grüneisen.†	Noyes and Melcher	Kohlrausch & Grüneisen.†	Foster‡.
18	2.0	112.2	112.1	109.7	109.5	124.8	124.6	94.3	94.1	93.8
	10.0	108.0	107.8	101.0	101.0	115.7	115.8	76.1	76.2	76.1
	20.0	......	......	......	......	......	......	67.5	67.7	....
	50.0	99.9	99.5	86.8	86.8	102.0	101.9	56.8	56.9	56.6
	100.0	94.6	94.3	79.1	78.9	95.0	94.9	49.8	49.7	49.5

Temperature.	Concentration.	Silver nitrate.		Magnesium sulphate.	
		Noyes and Melcher.	Kahlenberg.§	Noyes and Melcher.	Kahlenberg.§
100	2.0	353	335	302	305
	10.0	337	311	224	221
	40.0	312	282	160	163
	80.0	294	259	136	136
	100.0	289	257	130	130

*Kohlrausch und Steinwehr, Sitzungsber. preuss. Akad., 1902, 581.
†Kohlrausch und Steinwehr, Sitzungsber. preuss. Akad., 1904, 1215.
‡W. Foster, Phys. Rev., 8, 257 (1899).
§Kahlenberg, J. Phys. Chem. 5, 349, (1901).

42. CHANGE OF THE EQUIVALENT CONDUCTANCE WITH THE CONCENTRATION.

The empirical law of the variation of the conductance of silver nitrate, potassium sulphate, and barium nitrate with the concentration is shown by table 24, in which the values of the exponent n in the function $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$ are tabulated.

TABLE 24.—*Values of the exponent n in the function* $C(\Lambda_0 - \Lambda = K(C\Lambda)^n$.

Substance.	18°.	100°.	156°.	218°.	281°.	306°.
$AgNO_3$............	1.53	1.52	1.50	1.50	1.52	1.52
K_2SO_4	1.42	1.42	1.42	1.42	1.42	1.42
$Ba(NO_3)_2$........	1.50	1.50	1.50	1.50	1.50	1.50
$MgSO_4$............	1.43	....	....	....	....	....

It was shown in table 11, section 17, Part II, that the value of *n* for sodium and potassium chlorides lies between 1.40 and 1.50 at all temperatures, and it will be seen from this table that the same is true also for the tri-ionic salts, potassium sulphate and barium nitrate. This striking fact, which is in utter contrast with the requirements of the mass-action law, according to which the exponent should have the very different values 2 and 3 for these different types of salts does not seem to have been sufficiently considered in the discussion of the possible causes of the deviations. It is worthy of note also that the exponent has about the same value for the uni-univalent salt silver nitrate, which is very different chemically from the alkali-element chlorides, and that this is also true even for the bibivalent di-ionic salt magnesium sulphate at 18°. For the last salt we have not calculated the exponent at higher temperatures, owing to the large hydrolysis which doubtless exists.

Attention may also be called to the constancy throughout the whole range of temperature of the exponent *n* for each individual salt. This seems to indicate that even at the highest temperature the hydrolysis has not in any case become considerable. It should be mentioned, however, that in the case of potassium sulphate it was not possible to determine the value of the exponent nearer than 0.05 unit, owing to the fact that this salt, unlike the others, does not seem to conform completely to any exponential function of the type in question.

43. CHANGE OF THE EQUIVALENT CONDUCTANCE WITH THE TEMPERATURE.

The effect of temperature on the equivalent conductance values at zero concentration (the Λ_0 values) will be mainly considered in this section. Attention may first be called to the ratios given in table 25 of the Λ_0 values for silver nitrate, potassium sulphate, and barium nitrate to those for potassium chloride.

TABLE 25.—*Ratio of Λ_0 values to those for potassium chloride.*

Substance.	18°.	100°.	156°.	218°.	281°.	306°.
$AgNO_3$	0.89	0.89	0.91	0.95	0.96	0.95
K_2SO_4	1.02	1.10	1.14	1.29	1.45	1.54
$Ba(NO_3)_2$	0.90	0.93	0.96	1.02	1.11	1.16

It will be seen that with rising temperature the conductance of silver nitrate, like that of sodium chloride (see section 18, Part II), approaches the conductance of potassium chloride, thus furnishing another exemplification of the principle that the ratio of the specific velocities of the various ions approaches unity with rising temperature.

In the cases of the two tri-ionic salts the apparently abnormal phenomenon is observed that their equivalent conductance, though about equal to or less than that of potassium chloride at 18°, becomes much larger than it at the higher temperatures. The very large values of the ratios at 281° and 306°, especially for potassium sulphate, can not be caused by hydrolysis; for this would have an opposite effect, owing to the smaller equivalent conductance of the univalent ions thereby produced (for example, of the $OH^- + HSO_4^-$ ions which would replace the $SO_4^=$ ion): and at the lower temperatures (218° and below) appreciable hydrolysis does not exist, since the acids and bases involved have been shown by the measurements of Noyes and Eastman (section 97, Part VIII) to be too much ionized to admit of it. The real peculiarity in the results does not, however, consist in the large value of the ratio at the higher temperatures, but rather in the approximation of it to unity at the lower ones; for, since a bivalent ion, like Ba^{++} or $SO_4^=$, is in the same electric field, owing to its double charge, acted on by twice as large a force as a univalent ion, it would, provided it met with the same resistance, move with twice the velocity, and therefore have twice the equivalent conductance. The equivalent conductance of a completely ionized uni-bivalent salt would therefore approach 1.5 times that of a uni-univalent salt if the specific velocities of the various ions (that is, the velocities under unit electric force) approached equality. An approximation to this limiting value seems to be indicated in the case of potassium sulphate, and a change in the same direction is clearly shown by barium nitrate. That the equivalent conductances of the bivalent ions are so small at ordinary temperatures signifies, of course, a high resistance to their passage through the solution. This may arise from their being much hydrated; and the large increase in velocity with rising temperature may be due to a decrease in the hydration.

In order to show more clearly the relation between equivalent conductance and temperature for the individual substances, we have calculated the values of $\Delta\Lambda_0/\Delta t$ for the successive temperature intervals, and tabulated them in table 26, together with those for potassium and sodium chlorides already given in section 18, Part II.

TABLE 26.—*Temperature-coefficients of the equivalent conductance at zero concentration.*

Substance.	18–100°.	100–156°.	156–218°.	218–281°.	281–306°.
KCl	3.46	3.77	3.23	2.86	4.60
NaCl	3.09	3.44	3.31	3.33	4.40
$AgNO_3$	3.06	3.62	3.39	2.94	4.00
K_2SO_4	3.93	4.64	5.64	6.27	10.6
$Ba(NO_3)_2$	3.27	3.84	3.87	4.44	7.20

It will be seen that silver nitrate has temperature-coefficients which run parallel to those for potassium and sodium chlorides, and which, like the latter, pass through a maximum value somewhere in the neighborhood of 156°. The coefficients of potassium sulphate and barium nitrate, on the other hand, differ greatly from each other, and increase continuously with rising temperature.

With reference to the equivalent conductance values at the higher concentrations, mention need be made only of the fact that as shown in table 22, those for 80-milli-normal solutions have a maximum value at 281° in the case of silver nitrate, at 218° in the cases of potassium sulphate and barium nitrate, and at 100° in that of magnesium sulphate. This is, of course, due to a compensation of the effect of increasing migration-velocity by that of decreasing ionization.

44. IONIZATION-VALUES AND THEIR CHANGE WITH THE CONCENTRATION AND TEMPERATURE.

In table 27 are given the ratios (multiplied by 100) of the conductances at the various concentrations to that at zero concentration at each temperature. These ratios are at least an approximate measure of the percentage ionization of the substances, in those cases where the hydrolysis is not large and complex or intermediate ions are not formed, and provided the conductances at zero concentration can be regarded as correct. It is not probable that the hydrolysis is large enough at the higher concentrations to seriously vitiate this interpretation of the results, except in the case of magnesium sulphate at 100° and above. No definite information is available in regard to the existence at the higher temperatures of intermediate ions like KSO_4^- and $BaNO_3^+$; but the facts that transference determinations* have shown their absence in any considerable quantity at ordinary temperatures and that the functional relation between concentration and conductivity is identical at all temperatures (as was shown in section 42) make it probable that such ions do not exist in large quantity at the higher temperatures. Aside from these uncertainties in the interpretation of the conductivities at the higher concentrations, there is the possibility of considerable inaccuracy in some of the values adopted for zero concentration. This possibility exists especially in the case of magnesium sulphate at 100° and above, for which the Λ_0 values were derived from those for potassium sulphate and barium nitrate under the assumption that the magnesium and barium ions have equal migration-velocities. It may also exist to some extent in the case of potassium sulphate and barium nitrate

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*See Noyes, Z. phys. Chem., **36**, 79 (1901).

at 281° and 306°, owing to the possible effect of hydrolysis. The ionization-values for magnesium sulphate at 100°, 156°, and 218° are therefore to be regarded only as rough estimates, and those for potassium sulphate and barium nitrate at 281° and 306° as possibly in error by several per cent.

TABLE 27.—*The conductance ratio* (100 Λ/Λ_0) *and approximate percentage ionization.*

Substance.	Concentration.	18°.	100°.	156°.	218°.	281°.	306°.
Silver nitrate	0	100.0	100.0	100.0	100.0	100.0	100.0
	2.0	96.9	96.2	94.6	93.2	90.9	87.7
	10.0	93.3	91.8	88.8	86.3	81.8	76.8
	20.0	90.8	88.7	85.5	81.9	....	....
	40.0	87.5	84.9	81.2	76.8	70.5	63.8
	80.0	83.3	80.2	75.8	70.8	63.7	56.7
	100.0	81.7	78.8	....	....	....	....
Potassium sulphate	2.0	94.0	88.4	85	76	61	50
	10.0	87.2	80.3	75	63	47	37
	40.0	78.5	70.3	64	51	36	27
	80.0	73.2	64.8	58	45	31	23
	100.0	71.6	62.3	....	....	....	....
Barium nitrate	2.0	93.8	91.4	89	85	74	63
	10.0	86.7	83.6	80	74	59	47
	40.0	76.2	72.7	69	60	45	34
	80.0	70.1	66.9	62	53	38	....
	100.0	67.9	64.7	....	....	....	....
Magnesium sulphate	2.0	82.6	70.8	55	24	....	....
	10.0	66.7	52.4	35	13	....	....
	20.0	59.2	44.6	28	10	....	....
	40.0	52.0	37.5	23	8	....	....
	80.0	45.5	31.9	19	7	....	....
	100.0	43.7	30.4	....	....	....	....

With respect to the change of ionization with the concentration at any definite temperature, it will suffice to recall that the functional relation must be of a corresponding form to that between equivalent conductance and concentration, which was discussed in section 42, and again to emphasize the remarkable fact that the exponent in that function has nearly the same value for di-ionic and tri-ionic salts, and a value, moreover, which does not vary markedly with the temperature. Thus for the five substances, potassium chloride, sodium chloride, silver nitrate, potassium sulphate, and barium nitrate, at all temperatures between 18° and 306° inclusive, the ionization (γ) can be expressed by an equation $C(1-\gamma) = \text{const.} \times (C\gamma)^n$, in which n has values varying only between 1.40 and 1.52.

Assuming that the conductance-ratio may be regarded as at least an approximate measure of the ionization, certain conclusions in regard to the relation of the latter to temperature may be drawn from the results of table 27 considered in connection with those of potassium and sodium chlorides given in table 12 of section 19, Part II. To make these more evident we have brought together in table 28 the values of the percentage ionization as given by the ratio $100\Lambda/\Lambda_0$ for all these substances at a concentration of 0.08 normal.

TABLE 28.—*Percentage ionization* (100γ) *at* 0.08 *normal.*

Substance.	18°.	100°.	156°.	218°.	281°.	306°.
NaCl..........	85.7	83.2	81.2	77.7	70	63
KCl...........	87.3	82.6	79.7	77.3	72	64
$AgNO_3$.......	83.3	80.2	75.8	70.8	64	57
K_2SO_4	73.2	64.8	58	45	31	23
$Ba(NO_3)_2$.....	70.1	66.9	62	53	38	(28)
$MgSO_4$.......	45.5	32	19	7	..	..

It will be seen from this table that the ionization of the three di-ionic salts, sodium and potassium chlorides and silver nitrate, different as they are chemically, have not very far from the same ionization values throughout the whole range of temperature. The same is true of the two tri-ionic salts, potassium sulphate and barium nitrate. Thus the rule already deduced from the ionization values at ordinary temperatures that salts of the same ionic type have roughly the same degree of ionization also applies at high temperatures.

The principle that the ionization of salts at any definite concentration is smaller, the greater the product of the valences of the constituent ions, is an even more pronounced one at the higher temperatures. Thus at 218° the ionization of the uni-univalent salts in 0.08 normal solution is on the average 74 per cent, that of the unibivalent salts about 50 per cent, and that of the single bibivalent salt investigated only 7 per cent.

Most striking of all is the fact that the still more definite principle that the un-ionized fraction is directly proportional to the product of the valences of the ions* still holds true approximately when that fraction has become very large as it has at the higher temperatures. Table 29 shows under A the mean values of $100(1-\gamma)$ at 0.04 molal (and for the uni-univalent salts at 0.08 molal), and under B the ratios of these values to the product ($\nu_1\nu_2$) of the valences, for the salts of the three types included in table 28.

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*In regard to this, see A. A. Noyes, The Physical Properties of Aqueous Salt Solutions in Relation to the Ionic Theory, Congress of Arts and Science, St. Louis Exposition, **4**, 320 (1904); Technology Quarterly, **17**, 303 (1904); abstracted in Z. phys. Chem., **52**, 634 (1905).

TABLE 29.—*Un-ionized fraction in relation to valence-product.*

$\nu_1\nu_2$	Mols per liter.	18°.		100°.		156°.		218°.		281°.		306°.	
		A	B	A	B	A	B	A	B	A	B	A	B
1 x 1	0.04	12	12	15	15	17	17	20	20	25	25	31	31
1 x 1	0.08	15	15	18	18	21	21	25	25	31	31	39	39
1 x 2	0.04	28	14	34	17	40	20	51	25	65	32	74	37
2 x 2	0.04	55	14	68	17	81	20	93	23	..	..	..	..

It will be seen that the principle continues to hold, especially when the comparison is made at the same equivalent concentration, even when the ionization has become very small; thus it is only 26 per cent for the unibivalent salts at 306° and only 7 per cent for the bibivalent salt (magnesium sulphate) at 218°.

In correspondence with this principle, the rate of decrease of ionization with rising temperature for the individual substances is greater for the unibivalent than for the uni-univalent salts, and is still greater for the bibivalent salt magnesium sulphate. Moreover, the rate of decrease of ionization per degree increases rapidly with rising temperature, especially above 100°. The following values of $(-10^3\Delta\gamma/\Delta t)$, which represent the absolute decrease in percentage ionization produced by a rise in temperature of 10°, illustrate these statements.

TABLE 30.—*Temperature-coefficients of ionization* $(-10^3\Delta\gamma/\Delta t)$.

Substance.	18°-100°.	100°-156°.	156°-218°.	218°-281°.	281°-306°.
NaCl..........	0.30	0.36	0.56	1.30	2.6
KCl...........	0.57	0.52	0.39	0.86	3.1
$AgNO_3$..........	0.38	0.79	0.81	1.15	2.8
K_2SO_4..........	1.05	1.2	2.1	2.2	3.2
$Ba(NO_3)_2$.......	0.39	0.9	1.5	2.4	....

45. SUMMARY.

In this article have been presented (in table 22, section 41) values for the equivalent conductance of silver nitrate, potassium sulphate, and barium nitrate at six different temperatures lying between 18° and 306° and at concentrations between 0.002 and 0.08 or 0.1 normal. Similar values are given for magnesium sulphate up to still higher concentrations for four different temperatures extending up to 218°. From these by graphic extrapolation have been derived equivalent conductance values for zero concentration, which are proportional to the migration-velocities of the constituent ions. The ratios of the conductance at the various concentrations to that at zero concentration, which ratios represent approximately the degree of ionization, have been calculated (see table 27, section 44). Specific volume data for the more concentrated solutions have also been presented (in table 18, section 38).

A study of these data has led to the following conclusions:

(1) At all temperatures the equivalent conductance (Λ) and ionization (γ) of the two tri-ionic salts, potassium sulphate and barium nitrate, vary with the concentration according to approximately the same law as do those of silver nitrate and of the other two di-ionic salts, potassium and sodium chlorides, previously investigated. For, in the case of all these five salts, in order that functional relations of the form $C(\Lambda_0 - \Lambda) = \text{const.} \times (C\Lambda)^n$ or $C(1-\gamma) = \text{const} \times (C\gamma)^n$ may express the results, values varying only between 1.40 and 1.52 must be assigned to the exponent *n*, while according to the mass action law its value should be 2 for di-ionic and 3 for tri-ionic salts.

(2) The principle that the relative velocities of different ions acted upon by the same electric force approach equality with rising temperature is strikingly exemplified in the case of the bivalent $SO_4^{=}$ and Ba^{++} ions. Since bivalent ions owing to their double charge are acted upon by twice the electric force when in the same electric field, their equivalent conductance would become twice as great as that of univalent ions when the resistance to their motion through the solution was the same; and in this case the equivalent conductance of a completely ionized salt consisting of a univalent and a bivalent ion would become 1.5 times that of a uni-univalent salt. Now, our results show that at 18° the salts potassium suphate and barium nitrate have equivalent conductances at zero concentration which are 1.02 and 0.90 times respectively that of potassium chloride, but that at 306° the corresponding ratios are 1.54 and 1.16.

(3) The ionization values at all temperatures for silver nitrate agree within a few per cent with those previously derived (in Part II) for sodium and potassium chlorides; and the values for potassium sulphate and barium nitrate also agree with each other within a few per cent; thus confirming at high temperatures and for relatively small ionization the rule that most salts of the same ionic type have roughly the same degree of ionization.

(4) The ionization of all the salts investigated decreases steadily with rising temperature, the decrease being more rapid the higher the temperature and the greater the valences of the ions of the salt. Even where the ionization has become small, as it has at the higher temperatures, the simple principle still holds true approximately that the fraction of the salt un-ionized is proportional to the product of the valences of its ions.

PART V.

CONDUCTIVITY AND IONIZATION OF HYDROCHLORIC ACID, ACETIC ACID, AND SODIUM ACETATE UP TO 218°. HYDROLYSIS OF SODIUM ACETATE AND IONIZATION OF WATER AT 218°.

BY ARTHUR A. NOYES AND HERMON C. COOPER.

PART V.

CONDUCTIVITY AND IONIZATION OF HYDROCHLORIC ACID, ACETIC ACID, AND SODIUM ACETATE UP TO 218°. HYDROLYSIS OF SODIUM ACETATE AND IONIZATION OF WATER AT 218°.

46. OUTLINE OF THE INVESTIGATION.

In Parts II and III of this publication an apparatus and method have been described by which accurate measurements of the electrical conductance of aqueous solutions can be extended up to 306° or higher. This has made it possible to investigate at high temperatures such other physical properties and chemical reactions, as can be studied with the help of conductivity measurements. One of the most interesting of these is the phenomenon of the hydrolysis of salts into free acid and base — a phenomenon which is dependent in large measure on the degree of ionization of water itself, and from which, when supplemented by determinations of the ionization of the acid and base involved, this important quantity can be computed. Owing to the fact that the ionization of water increases very rapidly with rising temperature while the ionization of most weak acids and bases decreases, the hydrolysis of salts plays at high temperatures a much more prominent part than at ordinary ones and its effect must be taken into consideration even in the case of salts which at the ordinary temperature are not appreciably hydrolyzed. We have therefore undertaken an investigation in this direction.

The method employed for determining the hydrolysis is in principle that described first by Walker,* and later, in much more exact form by Bredig.† It consists in measuring the decrease of conductivity produced by adding to the salt solution, in which the salt is partially hydrolyzed, a sufficient quantity of the slightly ionized acid (or base) to reduce the degree of hydrolysis substantially to zero and in computing from this decrease and the previously determined difference in the mobility of the hydroxyl (or hydrogen) ion and the anion (or cathion) of the salt the fraction of the salt hydrolyzed. Thus, in the case of sodium acetate, the conductivity of this salt in its ordinary condition was first measured; then that of a solution of the salt of the same concentration containing also a considerable proportion of free acetic acid (which was varied in different experiments) was determined. The observed difference (after applying a small correction for the conductivity of the added acid in the presence of its neutral salt) evidently corresponds to the difference between the conductivity of the sodium hydroxide that exists free in the original solution and that of an equivalent quantity of sodium acetate. From the so-derived degree of hydrolysis and the ionization-constant of the acetic acid, the ionization-constant of water itself can be calculated with the help of the mass-action law, as has been shown by Arrhenius.*

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*Ztschr. phys. Chem., 4, 333 (1889). †Ztschr. phys. Chem., 13, 214, 321 (1894).

The determination of the hydrolysis of the single salt, sodium acetate, and the calculation from it of the ionization of water at any temperature involves, therefore, conductivity measurements of solutions at various concentrations of the following substances: (1) sodium acetate alone; (2) sodium acetate mixed with acetic acid (preferably in varying proportions); (3) acetic acid; (4) hydrochloric acid; (5) sodium chloride in very dilute solution (the last two being necessary in order to compute the conductivity of completely ionized acetic acid according to the relation $\Lambda_{0(HAc)} = \Lambda_{0(NaAc)} + \Lambda_{0(HCl)} - \Lambda_{0(NaCl)}$; and (6) sodium hydroxide in dilute solution. These measurements, except those with sodium hydroxide, have been made at a series of four temperatures, 18°, 100°, 156°, and 218°, by one of us (H. C. Cooper), those with sodium chloride at 218° being, in part, however, a repetition of the earlier ones of Noyes and Coolidge. Measurements with sodium hydroxide at the same temperatures have been made in this laboratory by Mr. Yogoro Kato; and these will be described in Part VI. All the data necessary for the calculations are therefore available.

Since the measurements with hydrochloric acid and acetic acid are the first ones made with acids at high temperatures, and since those with sodium acetate make possible a comparison of the behavior of this organic salt with that of the inorganic salts previously investigated, the results have a considerable interest of their own; and a large part of this article is devoted to the presentation and discussion of them.

Before considering these results, however, the apparatus and method used for the conductivity measurements and the preparation and standardization of the solutions must be described; and to this description the next two sections will be devoted.

47. APPARATUS AND METHOD OF PROCEDURE.

The apparatus used was substantially the same as that employed in the previous investigation of Noyes and Coolidge. (See Part II.) Only the small modifications made in it will be here described in detail.

THE CONDUCTIVITY CELL, OR BOMB.

The bomb itself was the same one that was used by these investigators. It was used without any modification in the first experiments. Somewhat later, in attempting to make measurements with dilute sodium acetate and hydrochloric acid at 218°, difficulty was met with in obtaining constant readings, apparently owing to adsorption by the lower electrode. The platinum-black was therefore removed from it (on April 4, 1904) by rubbing it with cotton and moist pumice. Later (on June 25, 1904), in order to diminish any contaminating influence of the electrode or quartz cup exerted upon the small quantity of liquid within the cup, the cup and the flat electrode within it were removed and replaced by a cylindrical electrode of an iridium-platinum alloy with 15 per cent iridium and an insulating cylinder of quartz.* This electrode was 9.7 mm. high and 7.2 mm. in diameter.

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*Ztschr. phys. Chem., 5, 17 (1890).

It was not found necessary to renew any of the parts of the bomb throughout the course of the work; and very little difficulty was experienced from leaks, which occurred only a few times and were then easily remedied.

THE CONDUCTIVITY MEASURING APPARATUS.

The conductivity was measured with an apparatus of the roller type described by Kohlrausch and Holborn† and furnished by Hartmann and Braun. The resistance coils of 1, 10, 100, 1,000, 10,000 ohms were of manganine. Heavy copper wire leads were used to within a few cm. of the slide wire and the heaters, the end connections being made of heavy flexible leads with brass connectors joining them to the slide wire and to the leads attached to the bomb. The entire lead resistance amounted to only 0.02 ohm.

The slide-wire was calibrated by the method of Strouhal and Barus, once just before the conductivity work was begun and again on June 1, 1904, the difference in the two cases, as well as the maximum error, being very slight. The corrections were, however, applied to the conductivity measurements. The resistance coils were compared with standard resistances, certified by the Deutsche phys.-technische Reichsanstalt.

INDUCTION COILS.

Two induction coils were used; at first a small one of the ordinary form was employed, and afterwards, in order to reduce the effect of ejection of material from the electrodes, a Nernst‡ string interrupter was used. The quality of the minimum afforded by this latter interrupter was satisfactory even with bright electrodes. In the case of all the measurements except those with sodium chloride, a commutating switch was introduced between the induction coil and the bridge, and the mean of the two readings taken.

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*Section 27, Part III. †Leitvermögen der Elektrolyte, 1898, p. 42, fig. 37.
‡Kohlrausch and Holborn, Leitvermögen der Elektrolyte, 1898, p. 29.

HEATERS.

The conductivity measurements were made at 18° and approximately 100°, 156°, and 218°. The first of these temperatures was secured with a bath of liquid xylene contained in a well-jacketed metal cylinder. The temperature was regulated by the observer, the bath being heated electrically by means of a resistance coil and cooled by a coil of lead pipe, through which cold water was passed. The bath was constantly stirred by a propeller. The temperature could be maintained constant to within 0.01°.

The 100° heater was a double-walled copper cylinder heated by steam, similar to that described in section 32, Part IV.

The 156° and 218° baths were of the form described in the article by Noyes and Coolidge.* Brombenzene and naphthalene were used as boiling substances, the latter substance proving very satisfactory throughout. The temperature of the brombenzene bath remained constant through several successive heatings, but in time a slight decomposition necessitated the substitution of fresh liquid. The same shielding devices for securing uniform temperature were employed as in the previous work.

THERMOMETERS.

Three different thermometers were used in the work — a 0–60° thermometer, reading directly to tenths, for the 18° bath, an ordinary Beckmann style thermometer for the 100° bath, a French mercurial 360° thermometer made by Alvergniat, No. 65650, for the two vapor baths. The 18° point of the first thermometer was determined by comparison with a standard Baudin thermometer. The steam point of the Beckmann thermometer was determined each time by introducing the thermometer into a boiling-point testing apparatus of the Regnault type immediately before or after each 100° measurement. The Alvergniat 360° thermometer was similarly calibrated for the 218° point at frequent intervals by immersion in a vapor bath of specially purified naphthalene of the type recommended by Crafts.† For the 156° point the bore was calibrated by the method recommended by Crafts and the value of the scale unit was determined from the interval between the steam and naphthalene points. The temperatures lying between the fixed points were reduced to the gas scale by using Crafts' table of corrections for French glass, our thermometer being of the same make as those used by him. For the boiling point of naphthalene, however, the result more recently obtained by Jaquerod and Wassmer ‡ was adopted.

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*Section 3, Part II.

†Am. Chem. J., **5**, 307-338 (1883-84).

‡J. chim. phys., **2**, 72 (1904).

METHOD OF PROCEDURE.

The procedure was substantially the same as that described by Noyes and Coolidge.* In the case of solutions which were liable to adsorption by the platinum, this effect was largely avoided by allowing the solution to remain in the bomb between the experiments (usually over night) and rinsing the bomb with solution only before introducing a fresh portion for a new experiment. In passing to a diluter solution, the bomb was first steamed out at 218° with the diluter solution instead of with water.

In the experiments with a platinized lower electrode, the air pressure within the bomb was reduced at the start to 2 cm. of mercury. In subsequent experiments with unplatinized electrodes, the measurement at 18° was made under atmospheric pressure and then the pressure was reduced to about 10 cm. of mercury before going on to the higher temperatures.

For each measurement of resistance, three different box resistances were used, generally in the order 100, 110, 111. These series of readings were made at 5-minute intervals, and the bomb was kept in the bath until three or more successive series of readings showed no progressive change.

In the case of all the solutions which showed any variation in the reading, the bomb was removed from the bath, shaken, and returned as quickly as possible, in order to determine whether there was any change in the solution around the electrode.

48. PREPARATION OF THE SUBSTANCES AND SOLUTIONS.

For the preparation of sodium chloride, pure commercial salt was twice reprecipitated from saturated solution with hydrochloric acid, filtered, washed, and ignited. Tests for potassium and for sulphate gave negative results. For potassium chloride, a Kahlbaum preparation was purified by reprecipitation from saturated solution in best water by pure hydrochloric acid and subsequent washing and ignition. A flame test showed no sodium.

The potassium chloride and sodium chloride solutions, except the 0.0005 normal sodium chloride solution, were prepared by weighing out a proper quantity of freshly ignited salt (corrected for the buoyancy of the air) and dissolving it in water in a graduated 2,000 or 500 c.cm. flask at 21°, the flask being so calibrated as to contain 2,000 or 500 grams of water at that temperature. The 0.0005 normal sodium chloride solution was made by diluting a 0.002 normal solution by means of a 500 c.cm. and a 2,000 c.cm. flask.

Hydrochloric acid was prepared by heating sodium chloride of the same quality as was used for preparing the sodium chloride solutions with sulphuric acid and absorbing the hydrochloric acid gas in pure water, after washing it by passing it through a bottle containing a little water. With the help of a specific gravity determination, two liters of approximately 0.1 normal hydrochloric acid were prepared (January 9, 1904) by dilution with pure water. The concentration of this 0.1 normal hydrochloric acid solution was determined by precipitating with silver nitrate and taking the mean of three analyses. One gram of solution was found to give 0.014519 gm. AgCl (*a. d.*,* 0.07 per cent). Some of the measurements (with tenth normal HCl) were made with a solution diluted from a hydrochloric acid solution carefully and independently prepared by Mr. Y. Kato. One gram of this latter solution gave 0.019675 gm. AgCl (*a. d.*, 0.03 per cent).

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*Section 6, Part II.

For the preparation of pure sodium acetate, about 500 grams of a Kahlbaum sample were crystallized from water, after the salt had been tested with negative results for potassium and the common acids. The salt was partially dried with filter paper. An approximately tenth-normal solution was prepared (March 10, 1904) and analyzed by evaporating it with hydrochloric acid in a platinum dish, and gently igniting and weighing the residue of sodium chloride. One gram of solution gave on the average, 0.005732 gm. NaCl (*a. d.*, 0.09 per cent). A second solution was similarly prepared June 6, 1904, and analyzed three times, twice immediately after its preparation and again on August 1, 1904. One gram of solution gave (1) 0.005588 gm. (2) 0.005592 gm. (3) 0.005601 gm. NaCl or as the average 0.005594 gm. (*a. d.*, 0.08 per cent).

For acetic acid some Kahlbaum "Eisessig" was subjected three times to fractional freezing in a specially devised apparatus, care being taken to exclude moisture. The liquid obtained was then rectified by distillation, about one-tenth being rejected. From the purified substance an approximately tenth-normal acetic acid was prepared (on May 12, 1904). Qualitative tests for sulphate and chloride gave negative results. The solution was then standardized against a barium hydroxide solution whose strength was determined by titration against two solutions of hydrochloric acid which had been independently standardized by precipitating with silver nitrate and weighing the silver chloride. One gram of solution was found to contain 0.006105 gm. acetic acid ($C_2H_4O_2$) by titration with one of the solutions and 0.006097 gm. by titration with the other, or, as a mean, 0.006101 gm. acetic acid.

The more dilute solutions of hydrochloric acid, sodium acetate and acetic acid were prepared by weighing out a definite amount of the stock solution and either diluting to the mark in a graduated flask or adding a known weight of water.

**a. d.* signifies the average deviation of the separate values from the mean.

The water used in the preparation of the stock solution had a specific conductance of less than 1.1×10^{-6}. That used for preparing the more dilute solutions had in almost all cases a specific conductance of $0.75 - 0.95 \times 10^{-6}$.

49. SYSTEMATIC ERRORS AND THEIR ELIMINATION.

The possible errors affecting the conductivity values and their elimination or correction have been fully discussed in section 10, Part II. It is therefore necessary only to refer to a few modifications of the corrections applied and to some new difficulties met with in the experiments.

VOLATILIZATION OF SOLVENT.

The correction for the quantity of solvent in the vapor-space in the bomb was applied in the case of the non-volatile solutes as before, it being calculated from the known volume of the vapor in the bomb and its specific volume interpolated or extrapolated from the data of Zeuner* which extend up to 200°. The correction requires an increase of the concentration of 0.01 per cent at 100°, 0.03 per cent at 156°, and 0.02 per cent at 218° in the case of our experiments. Although certainly less than the other errors it was always applied at 156° but not at the other temperatures.

VOLATILIZATION OF SOLUTE.

In the case of the acetic and hydrochloric acid solutions the correction for the vapor-space should also take into account the possible volatility of these solutes. In these cases the total correction for volatilized solvent and solute was experimentally determined at 218° by varying the quantity of solution placed in the bomb and measuring the conductances. From the variations of these with the known variations of vapor-space the correction for the vapor-space existing in the ordinary measurements could be readily calculated. Thus, for three different volumes of a 0.01017 normal acetic acid placed in the bomb, the vapor-spaces and conductances at 218° were as follows:

Vapor-space (cubic centimeters)..	1.5	11.1	25.4
Specific conductance $\times 10^6$........	447.3	447.8	448.5

It is evident that since 24 c.cm. of vapor-space cause an increase in the conductance of 0.27 per cent, that produced by the 1.5 c.cm. usually present would be about 0.02 per cent, which is the magnitude of the correction for the solvent alone, indicating that this solute does not volatilize appreciably. The same result was obtained with hydrochloric acid.

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*Landolt-Börnstein-Meyerhoffer, Tabellen, p. 127 (1905).

CONDUCTANCE OF THE WATER.

A correction was applied in the case of the two salts (but not in that of the two acids) for the conductance of the impurities in the water. This will be fully described in section 51, in connection with the data upon which it is based.

INCONSTANT BRIDGE READINGS.

No special trouble was encountered in the sodium chloride measurements. It was observed, however, in working with the diluter hydrochloric acid solutions that the bridge readings at 18°, and to a less extent at other temperatures, shifted rapidly when the current was kept on, the displacement being generally in the direction of increasing conductivity. The shifting reached a limit in about three minutes, but on discontinuing the current for a minute or two the reading returned to approximately its original value. It was considered likely that this was due to the ejection by the alternating current of solute which had been adsorbed by the lower electrode. It was not permissible to adopt the final reading, since the effect of ejection would be to concentrate the solution within the cup; and the initial reading could not be accurately determined. It was found that the shifting of the reading was greater, the louder the tone of the induction coil. A Nernst string interrupter, with low vibration frequency, was therefore substituted for the ordinary induction coil. The total shifting with the string interrupter was much less, and it took place so slowly that no difficulty was experienced in making a satisfactory reading. Except at the highest resistances measured the minimum with this interrupter was very good.

In working with the sodium acetate and the 0.0005 normal hydrochloric acid solution great difficulty was experienced, when either induction coil was employed, in securing constant readings at 218°, Cell 1 (see section 50) being then in use. Even after sufficient time had elapsed for the bomb to acquire the temperature of the bath, successive readings made during a half hour exhibited an irregular, somewhat oscillatory shifting through several centimeters on the bridge in the direction of decreased conductivity. If instead of reducing the pressure in the air space originally to 2 cm. of mercury as had been the practice, the air was allowed to remain in the bomb, the direction of shifting was reversed, these tests being made with a 0.01 normal sodium acetate solution. It was not possible to find an intermediate pressure which afforded constant readings. The effect of removing and shaking the bomb in the usual manner was to cause partial reversion towards the original reading, but not to prevent the recurrence of shifting. To see whether the shifting was due to uneven temperature some experiments were made, such as altering the level of the vapor in the bath and the manner of shielding, but with negative results. The removal of the platinum-black from the electrode almost entirely obviated this trouble, however, for the subsequent bridge-readings with sodium acetate and dilute hydrochloric acid at 218° were constant to within 0.2 to 0.3 mm. for a sufficient period. The pressure was reduced to 2 cm. previous to these measurements, as before. The change in reading was apparently due either to formation of bubbles on the electrode, or to an adsorption effect, but its cause could not be fully determined.

The use of a polished lower electrode (in Cell II) gave rise, however, to a similar difficulty under other conditions, namely, to a shifting of the bridge-reading in the direction of decreased conductance at 18° and to a less extent at higher temperatures. This was found to be due to the formation of bubbles and was obviated at 18° by postponing evacuation of the air space in the bomb till after the measurement at that temperature had been made. As a similar effect was observed to some extent at 100° and 156°, the air pressure was thereafter reduced only to about 12 cm. before the measurements at the three higher temperatures. The subsequent measurements proceeded satisfactorily, the same method being followed also after the introduction of the cylindrical electrode (Cell III). The air pressure that obtains in the bomb at 218°, for the usual volume of liquid, after a reduction of the pressure to 12 cm. at 18°, is only about two atmospheres, which does not affect the conductance to a considerable extent.

In order to diminish the adsorption, the rinsing of the bomb with water was omitted in the case of hydrochloric acid, acetic acid, and sodium acetate, and a portion of the solution to be measured was left in the cell for some hours previous to the experiment, in order to thoroughly saturate the electrode, a new portion of the same solution being introduced just before the measurements were made.

The experiments with sodium acetate were at first conducted with the quartz cup in the bomb. The readings with the solutions of it diluter than tenth-normal were not as constant as with other solutes. It was thought that the inconstancy might be due to a contamination of the solution by its attacking the quartz cup and a consequent concentration of the solution within the cup. This difficulty was apparently obviated (cell III) by the introduction of the new form of electrode and quartz insulator as described in section 47.

INSTRUMENTAL ERRORS.

In working with dilute solutions of hydrochloric acid it was found that commutating the current from the secondary coil gave a difference of reading of 0.1 — 0.4 mm. The coil was tested with known resistances and found to show an asymmetric reading only with the higher resistances, an error of 0.1 per cent or more being involved when the resistance exceeded 5,000 ohms. This error was corrected for, however, by taking double commutated readings in all such cases and finding the mean. It was found that commutating the telephone had no effect even with the highest resistances used.

In the measurement of very high resistances (those above 10,000 ohms) the proximity of the induction coil to the bridge was found to have an influence on the reading, if the distance was less than 40 cm. Such proximity was therefore avoided.

50. CONDUCTANCE-CAPACITY OF THE APPARATUS.

The conductance-capacity was calculated from measurements made in the bomb at 18° of the conductance of various known solutions of potassium chloride and sodium chloride and from the values of the equivalent conductance of these salts as given by Kohlrausch and Maltby.*

In the course of the work three different values of the conductance-capacity were used, corresponding to the changes made in the lower electrode. In all the measurements made prior to April 4, 1904, the bomb was used as it was left by Noyes and Coolidge, in which form it will be designated cell I. On that date the platinizing was mechanically removed from the electrode, which caused a slight change in the capacity, the new value of which (cell II) was used in connection with all measurements between April 4, and June 25, 1904. The quartz cup was then removed from the bomb and a cylindrical electrode substituted for the flat one. The new conductance capacity (cell III) then obtained is that used in calculating all the measurements made subsequently to June 25, 1904.

The following table shows the actual conductance at 18° of the solutions diminished by that of the water, and the conductance-capacities calculated therefrom. The conductances expressed in reciprocal ohms are given in the table multiplied by 10^6. The concentration is expressed in milli-equivalents per liter at 18°. The conductance-capacity is, as usual, the factor by which the observed conductance must be multiplied to give the specific conductance. Each of the measurements was made upon separate, freshly prepared solutions.

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*Wissensch. Abhandlungen phys.-techn. Reichsanstalt, **3**, 210 (1900). See also Landolt-Börnstein-Meyerhoffer, Tabellen, p. 744 (1905).

TABLE 31.—*Conductance-capacity.—Data and final values.*

Date.	Cell No.	Salt.	Concentration at 18°.	Conductance × 10^6.	Conductance-capacity.	
					Separate values.	Final values.
1903						
Nov. 20.......	I	NaCl....	9.999	1038.1	0.9819	......
1904						
Jan. 20.......		NaCl....	9.995	1039.9	0.9799	......
Jan. 21.......		NaCl....	100.52	9440	0.9800	......
Jan. 22.......		KCl.....	99.77	11400	0.9804	......
Jan. 22.......		NaCl....	99.86	9361	0.9816	0.9808
June 11.......	II	KCl.....	9.990	1242.7	0.9842	......
June 11......		KCl.....	49.95	5865	0.9858	......
June 11.......		NaCl....	9.992	1034.0	0.9851	0.9850
June 29.......	III	NaCl....	9.993	6856	0.14860	......
June 29.......		KCl.....	9.990	8233	0.14856	......
July 12.......		KCl.....	4.996	4194	0.14820	......
July 12.......		KCl.....	5.002	4197	0.14827	......
July 12.......		KCl.....	9.999	8246	0.14845	0.14842

The variation of these values of the conductance-capacity with the temperature was computed upon the basis and in the manner described in section 36, Part IV. The percentage corrections to be applied to them at the various temperatures are as follows:

	100°	156°	218°
Cells I and II................	—0.14	—0.25	—0.39
Cell III	—0.10	—0.18	—0.26

51. THE WATER CORRECTION.

CONDUCTANCE OF THE WATER.

In order to determine the conductance of the impurities in the water under the conditions of the experiments, water having about the same conductance as that used in making up the solutions was placed in the bomb, which had been previously twice heated to 218° with fresh portions of conductivity water to remove adsorbed substance. The conductance was measured at 18° and the bomb was heated in each of the various baths for the length of time usual in the measurements, being finally brought back in the reverse order to 18°. Table 32 contains the results of two such experiments, which served as the basis for the water correction.

In the case of the measurements with sodium chloride and sodium acetate (both with and without acetic acid added) the mean value here tabulated of the conductance of the water corresponding to the same stage of the experiment was subtracted from the measured conductance of the solution (except that in the few cases where the solutions were prepared from water having a specific conductance less than 0.75 or greater than 0.95×10^{-6} these corrections were varied in the ratio of that conductance to 0.85×10^{-6}, which was the conductance of the water used in the two experiments before its introduction into the bomb). No correction for the impurities in the water was applied to the measured conductances of the hydrochloric acid, since their effect is ordinarily to decrease by an indefinite amount the conductance of a solution of a strong acid rather than to increase it. In the case of acetic acid (and of sodium acetate with acetic acid added) the effect of the impurities would depend on their nature: bases (*e. g.*, ammonium hydroxide) and salts (*e. g.*, ammonium carbonate, sodium silicate) would increase the conductance of the solution by an amount equal to or greater than their own conductance, but very weak acids (for example, carbonic or silicic) owing to the reduction of their ionization would scarcely influence it at all. Since the water used was distilled from an alkaline solution (of permanganate) and was scarcely exposed to the atmosphere, it seems most probable that the impurities present are basic or saline; and therefore that it is best to subtract the conductance of the water. It has seemed advisable, however, to apply this correction to the final rather than to the separate values, and to give for comparison both the corrected and uncorrected results.

TABLE 32.—*Actual conductance of the water.*

	Conductance × 10^6.						
	18°.	100°.	156°.	218°.	156°.	100°.	18°.
Dec. 16, 1903	1.056	3.07	5.14	7.30	6.00	4.80	2.03
Mar. 12, 1904	0.854	3.11	5.45	7.35	5.93	4.28	1.67
Mean	0.955	3.09	5.30	7.32	5.97	4.54	1.85
Specific conductance × 10^6	0.937	3.03	5.18	7.15	5.84	4.45	1.82

52. CONDUCTIVITY DATA FOR SODIUM CHLORIDE, HYDROCHLORIC ACID, ACETIC ACID, AND SODIUM ACETATE.

The following table contains the direct results of the observations and the equivalent conductances computed from them. The first column gives the date of the experiment; the second, the cell-number of the conductivity vessel; the third, the concentration at 4° in milli-equivalents per liter (the number of milli-equivalents being based upon the atomic weights referred to oxygen as 16.000 and the weights being reduced to vacuo); the fourth, the temperature on the hydrogen-gas scale at which the conductance was measured; the fifth, the concentration at the temperature ot the measurement, calculated by dividing the concentration at 4° by the ratio of the specific volume of the solution at that temperature to its specific volume at 4°*, and applying the correction at 156° for the vapor space;

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*The specific-volume ratio at 100° and 156° was assumed to be identical with that for pure water. At 100° this value is 1.0432 according to Matthiessen and Rosetti; at 156° it is 1.0976, interpolated graphically from Hirn's values [Ann. chim. phys. (4), 10, 32 (1867)] at 140.17°, 151.00°, and 160.68° after correcting them to the pressures of saturated aqueous vapor with the help of the compression-coefficient of water, derived by extrapolation from the data of Pagliani and Vincentini which extend only to 100° [Landolt-Börnstein-Meyerhoffer, Tabellen 60 (1905)].

the sixth, the measured conductance in reciprocal ohms, multiplied by 10^6 and corrected for the instrumental errors (those in the slide wire and the resistance coils) and for the lead resistance; the seventh, the conductance-capacity of the vessel (the values being omitted when identical with those in a preceding experiment); the eighth, the equivalent conductance calculated from the value of the conductance in the sixth column by applying (in the case of the two salts) the water-correction (see section 51), multiplying by the conductance-capacity in the seventh column, and dividing by the concentration given in the fifth column.

TABLE 33.—*The conductivity data.*

SODIUM CHLORIDE.

Date.	Cell No.	Concentration at 4°.	Temperature, $t°$.	Concentration at $t°$.	Conductance × 10^6.	Conductance capacity.	Equivalent conductance.
1	2	3	4	5	6	7	8
1904 Jan. 4........	I	0.5003	18.00	0.4996	55.62	0.9808	107.34
			100.26	0.4795	177.62	0.9794	356.5
			156.3	0.4559	260.38	0.9783	547.5
			222.3	0.4190	331.4	0.9770	755.5
			156.5	0.4558	261.36	0.9783	548.3
			100.30	0.4795	179.34	0.9794	357.0
			18.00	0.4996	56.48	0.9808	107.30
Jan. 5........	I	0.5003	18.00	0.4996	55.78	......	107.65
			100.38	0.4795	178.03	......	357.3
			157.2	0.4555	263.3	......	554.3
			220.7	0.4201	334.1	......	760.1
			158.5	0.4548	272.4	......	573.2
			100.15	0.4796	185.80	......	370.2
			18.00	0.4996	59.45	......	113.1
Jan. 8........	I	0.5002	18.00	0.4996	55.94	......	107.61
			99.68	0.4797	177.24	......	354.3
			156.15	0.4559	260.8	......	546.2
			216.9	0.4224	327.0	......	736.1
			156.7	0.4556	262.6	......	548.6
			99.57	0.4797	179.63	......	355.6
			18.00	0.4996	57.28	......	108.17
Jan. 9........	1	0.5002	18.00	0.4996	55.86	......	107.46
			216.6	0.4226	325.9	......	733.1
1903 Nov. 28......	I	2.0009	18.07	1.9981	215.81	......	105.47
			218.65	1.6850	1,271.9	......	733.2
Dec. 17......	I	2.0009	18.00	1.9981	216.19	......	105.66
			99.76	1.9185	686.1	......	348.7
			157.15	1.8215	1,009.5	......	539.4
			220.8	1.6796	1,268.3	......	733.5
			158.0	1.8199	1,016.7	......	543.3
			99.86	1.9184	691.1	......	350.5
			18.00	1.9981	217.87	......	106.05
Dec. 18......	I	2.0009	18.00	1.9981	215.70	......	105.41
			100.19	1.9174	689.0	......	350.3
			158.8	1.8184	1,018.8	......	545.3
			221.0	1.6790	1,273.2	......	736.6
			160.1	1.8160	1,030.4	......	551.9
			100.29	1.9177	695.4	......	352.8
			18.00	1.9981	218.64	......	106.43

TABLE 33.—*The conductivity data*—Continued.

SODIUM CHLORIDE.

Date.	Cell No.	Concentration at 4°.	Temperature, t°.	Concentration at t°.	Conductance $\times 10^6$.	Conductance capacity.	Equivalent conductance.
1	2	3	4	5	6	7	8
1903							
Nov. 17......	I	10.013	18.07	9.999	1,041.4	......	102.04
			99.72	9.601	3,288	......	335.1
			155.5	9.130	4,777	......	511.2
			218.5	8.434	5,967	......	690.1
			155.75	9.127	4,786	......	512.3
			99.68	9.601	3,294	......	335.4
			18.07	9.999	1,048.5	......	102.63
Nov. 19......	I	10.013	18.07	9.999	1,040.3	......	101.93
			100.30	9.597	3,299	......	336.3
Nov. 20......	I	10.013	18.07	9.999	1,040.7	......	101.97
Nov. 23......	I	10.013	18.07	9.999	1,041.5	......	102.05
			99.81	9.600	3,292	......	335.5
			155.65	9.128	4,816	......	515.5
			218.6	8.433	5,969	......	690.5
			155.5	9.130	4,777	......	511.2
			18.07	9.999	1,044.8	......	102.27
1904							
Jan. 20......	I	10.009	18.00	9.995	1,041.5	......	102.09
			100.14	9.594	3,295	......	336.0
			157.2	9.111	4,810	......	515.8
			216.9	8.450	5,936	......	685.2
			157.9	9.104	4,825	......	517.7
			100.05	9.594	3,302	......	336.6
			18.00	9.995	1,041.9	......	102.03
HYDROCHLORIC ACID.							
1904							
Feb. 10......	I	0.4991	18.00	0.4985	190.77	0.9808	375.4
			100.17	0.4784	408.8	0.9794	836.8
			158.5	0.4538	497.5	0.9783	1,072.8
Feb. 12......	I	0.4996	18.00	0.4989	191.09	......	375.7
			100.16	0.4789	408.4	......	835.4
			158.4	0.4542	494.4	......	1,065.0
			218.6	0.4208	532.4	0.9770	1,236.2
			159.3	0.4538	500.8	......	1,079.6
			100.08	0.4789	408.1	......	834.5
			18.00	0.4989	190.53	......	374.6
Feb. 13......	I	0.4996	18.00	0.4989	190.77	......	375.0
Feb. 15......	I	0.4996	18.00	0.4989	190.77	......	375.0
Mar. 15......	I	0.4442	18.00	0.4436	169.04	......	373.8
			217.7	0.3746	475.7	......	1,240.4
			18.00	0.4436	168.69	......	373.0
Mar. 16......	I	0.4992	18.00	0.4985	190.15	......	374.1
			99.81	0.4786	406.4	......	831.6
			156.8	0.4546	493.5	......	1,062.3
			217.9	0.4209	533.1	......	1,237.5
			157.3	0.4543	495.7	......	1,067.6
			99.85	0.4786	408.2	......	835.3
			18.00	0.4985	190.15	......	374.1

TABLE 33.—*The conductivity data*—Continued.

HYDROCHLORIC ACID.

Date. 1	Cell No. 2	Concentration at 4°. 3	Temperature, $t°$. 4	Concentration at $t°$. 5	Conductance × 10^6. 6	Conductance capacity. 7	Equivalent conductance. 8
1904							
Apr. 8.......	II	0.4977	18.00	0.4970	189.65	0.9850	375.8
			100.05	0.4662	406.4	0.9836	837.9
			156.3	0.4534	493.3	0.9825	1,068.5
			218.1	0.4195	533.0	0.9811	1,246.7
			156.3	0.4534	494.3	......	1,071.1
			100.01	0.4662	407.0	......	839.1
			18.00	0.4970	189.79	......	376.1
Apr. 9.......	II	0.4977	18.00	0.4970	189.67	......	375.9
			99.90	0.4771	406.1	......	837.1
			156.1	0.4535	492.7	......	1,067.5
			217.9	0.4196	533.2	......	1,246.7
			156.2	0.4535	493.8	......	1,069.8
			99.76	0.4772	406.1	......	837.0
			18.00	0.4970	189.79	......	376.1
Apr. 15......	II	0.4995	18.00	0.4988	190.37	......	375.9
			99.90	0.4789	406.9	......	835.8
Apr. 16......	II	0.4995	18.00	0.4988	190.20	......	375.6
			99.60	0.4790	406.7	......	835.1
			217.8	0.4212	534.0	......	1,243.8
Feb. 16......	I	1.9997	18.00	1.9970	761.2	0.9808	373.8
			99.57	1.9176	1,616.3	0.9794	825.5
			156.8	1.8210	1,956.6	0.9783	1,051.2
			217.6	1.6867	2,112.4	0.9770	1,223.3
			157.5	1.8197	1,965.4	......	1,056.8
			99.59	1.9176	1,617.3	......	826.0
			18.00	1.9970	761.5	......	374.0
Feb. 17......	I	1.9997	18.00	1.9970	760.5	......	373.5
			99.85	1.9173	1,616.6	......	825.7
			157.8	1.8192	1,960.8	......	1,054.5
			218.2	1.6856	2,097.3	......	1,215.9
			157.9	1.8190	1,962.4	......	1,055.6
			99.87	1.9172	1,616.0	......	825.5
			18.00	1.9970	759.4	......	373.0
Feb. 18......	I	1.9997	18.00	1.9970	760.6	......	373.5
			218.7	1.6839	2,106.0	......	1,221.9
			18.00	1.9970	761.2	......	374.8
Feb. 20......	I	9.994	18.00	9.981	3,747	......	368.2
			100.34	9.578	7,919	......	809.8
			157.5	9.094	9,514	......	1,023.5
			218.9	8.413	10,109	......	1,173.9
			157.8	9.092	9,530	......	1,025.5
			100.36	9.578	7,924	......	810.2
			18.00	9.981	3,743	......	367.8
Feb. 23......	I	9.994	18.00	9.981	3,752	......	368.7
			99.75	9.583	7,904	......	807.8
			156.8	9.101	9,506	......	1,021.9
			217.8	8.428	10,145	......	1,176.1
			156.4	9.105	9,473	......	1,017.9
			99.64	9.583	7,892	......	806.6
			18.00	9.981	3,736	......	367.2
Feb. 24......	I	9.994	18.00	9.981	3,748	......	369.3
			217.1	8.435	10,114	......	1,171.3
			18.00	9.981	3,747	......	368.2

TABLE 33.—*The conductivity data*—Continued.

HYDROCHLORIC ACID.

Date.	Cell No.	Concentration at 4°.	Temperature, t°.	Concentration at t°.	Conductance × 10^6.	Conductance capacity.	Equivalent conductance.
1	2	3	4	5	6	7	8
1904							
Mar. 18......	I	100.66	18.00	100.52	35,910	......	350.4
			99.78	96.51	74,370	......	754.7
			156.2	91.73	87,570	......	934.0
			217.6	84.91	90,450	......	1,040.7
			156.2	91.72	87,620	......	934.8
			99.57	96.53	74,410	......	755.0
			18.00	100.52	35,950	......	350.8
Mar. 21......	I	100.66	18.00	100.52	35,900	......	350.3
			100.26	96.48	74,490	......	756.2
			157.3	91.62	87,740	......	936.9
			218.7	84.76	90,220	......	1,039.9
			157.8	91.57	87,750	......	937.5
			100.27	96.48	74,560	......	756.9
			18.00	100.52	35,950	......	350.8
SODIUM ACETATE.							
Apr. 23......	II	0.5008	18.00	0.5002	39.25	0.9850	75.82
			100.36	0.4800	136.77	0.9836	275.3
			156.4	0.4563	209.42	0.9825	441.9
			218.6	0.4218	274.8	0.9811	625.7
			156.5	0.4562	207.30	......	436.1
			100.27	0.4800	136.71	......	272.8
			18.00	0.5002	39.45	......	74.83
Apr. 26......	II	0.4988	18.00	0.4981	39.32	......	76.28
			99.79	0.4782	136.28	......	275.3
			156.0	0.4545	208.42	......	441.4
			217.8	0.4206	275.3	......	628.7
			156.1	0.4545	206.87	......	436.9
			99.81	0.4782	136.01	......	272.4
			18.00	0.4981	39.46	......	75.17
Apr. 27......	II	0.5015	18.00	0.5008	39.48	......	75.80
			100.03	0.4808	137.08	......	274.2
			156.3	0.4569	209.77	......	439.7
			218.1	0.4227	277.7	......	627.7
			156.5	0.4568	208.55	......	435.7
			100.05	0.4808	137.40	......	271.9
			18.00	0.5008	40.00	......	75.09
Apr. 12......	II	1.9903	18.00	1.9876	149.80	......	73.77
			99.51	1.9087	518.9	......	265.9
			156.8	1.8124	790.9	......	425.9
			155.7	1.8143	785.2	......	422.0
			99.60	1.9086	520.0	......	265.7
			18.00	1.9876	151.47	......	74.16
Apr. 20......	II	1.9980	18.00	1.9953	151.61	......	74.57
			99.50	1.9160	521.8	......	266.9
			155.3	1.8222	790.6	......	424.6
			217.3	1.6861	1,036.5	......	600.3
			155.3	1.8222	789.3	......	423.6
			99.57	1.9160	521.5	......	266.4
			18.00	1.9953	151.63	......	74.30

TABLE 33.—*The conductivity data*—Continued.

SODIUM ACETATE.

Date. 1	Cell No. 2	Concentration at 4°. 3	Temperature, t°. 4	Concentration at t°. 5	Conductance × 10⁶. 6	Conductance capacity. 7	Equivalent conductance. 8
1904							
Apr. 21......	II	1.9980	18.00	1.9953	151.57	......	74.55
			99.94	1.9154	523.3	......	267.8
			156.0	1.8209	792.5	......	425.9
			218.1	1.6840	1,036.3	......	601.2
			156.1	1.8207	791.8	......	425.4
			100.07	1.9153	523.6	......	267.6
			18.00	1.9953	151.63	......	74.30
July 14......	III	1.9985	18.00	1.9958	1,008.0	0.14842	74.52
			156.4	1.8207	5,280	0.14815	426.8
			217.9	1.6850	6,883	0.14803	601.1
			18.00	1.9958	1,010.3	......	74.24
Mar. 24......	I	10.002	18.00	9.998	723.7	0.9808	70.98
			100.40	9.585	2,494.0	0.9794	254.6
			157.3	9.104	3,751	0.9783	402.6
			156.9	9.107	3,740	......	401.1
			100.36	9.587	2,496.0	......	254.4
			18.00	9.998	724.3	......	70.95
Mar. 25......	I	10.002	18.00	9.988	723.5	......	70.96
			100.20	9.587	2,485	......	253.6
			156.8	9.108	3,733	......	400.4
			156.7	9.109	3,727	......	399.7
			100.04	9.588	2,487	......	253.7
			18.00	9.988	725.5	......	71.06
June 10......	II	10.000	18.00	9.986	722.1	0.9850	71.14
			100.20	9.585	2,483.9	0.9836	254.6
			156.1	9.113	3,729	0.9825	401.5
			156.2	9.112	3,724	......	400.9
			100.09	9.585	2,478.9	......	254.0
			18.00	9.986	723.4	......	71.18
June 27......	III	9.992	18.00	9.978	4,717	0.14842	70.07
			156.1	9.105	24,289	0.14815	395.1
			217.9	8.424	31,390	0.14803	551.4
			18.00	9.978	4,812	......	71.40
July 5.......	III	9.984	18.00	9.971	4,791	......	71.23
			155.5	9.103	24,661	......	400.8
			217.6	8.421	31,730	......	556.9
			18.00	9.971	4,796	......	71.21
July 6.......	III	10.006	18.00	9.992	4,808	......	71.33
			155.9	9.120	24,534	......	398.0
			217.7	8.438	31,445	......	550.8
			18.00	9.992	4,815	......	71.34
July 7.......	III	10.018	18.00	10.004	4,807	......	71.23
			156.0	9.130	24,600	......	398.6
			217.8	8.447	31,480	......	550.8
			18.00	10.004	4,824	......	71.39
July 11.......	III	10.001	18.00	9.988	4,811	......	71.40
			155.8	9.116	24,552	......	398.4
			217.4	8.438	31,490	......	551.5
			18.00	9.988	4,823	......	71.49
June 16......	II	76.06	18.00	75.95	4,904	0.9850	63.59
			99.98	72.91	16,504	0.9836	222.66
			156.4	69.29	24,408	0.9825	346.0
			218.0	64.11	30,350	0.9811	464.4

TABLE 33.—*The conductivity data*—Continued.

Date.	Cell No.	Concentration at 4°.	Temperature, t°.	Concentration at t°.	Conductance $\times 10^6$.	Conductance capacity.	Equivalent conductance.
1	2	3	4	5	6	7	8
SODIUM ACETATE.							
1904							
June 23......	II	76.22	18.00	76.11	4,927	......	63.75
			100.15	73.06	16,578	......	223.21
			218.3	64.22	30,390	......	464.1
			156.3	69.44	24,426	......	345.5
			100.15	73.06	16,556	......	222.90
			18.00	76.11	4,923	......	63.68
June 14......	II	95.55	18.00	95.42	6,034	......	62.28
			100.12	91.59	20,303	......	218.17
			156.2	87.06	29,900	......	337.4
			218.2	80.52	37,020	......	451.0
			156.1	87.07	30,050	......	339.0
			100.05	91.59	20,318	......	218.19
			18.00	95.42	6,050	......	62.43
ACETIC ACID.							
May 20.......	II	10.302	18.00	10.288	150.07	0.9850	14.369
			99.40	9.880	256.4	0.9836	25.53
			155.4	9.394	223.41	0.9825	23.37
			217.4	8.692	146.85	0.9811	16.577
			155.6	9.393	223.22	......	23.35
			99.64	9.878	256.5	......	25.55
			18.00	10.288	149.87	......	14.349
May 24.......	II	10.034	18.00	10.020	148.11	......	14.560
			99.90	9.620	253.3	......	25.91
			156.1	9.143	220.84	......	23.73
			217.9	8.460	146.53	......	16.995
			18.00	10.020	148.02	......	14.550
June 2.......	II	10.003	18.00	9.990	147.90	......	14.583
			100.08	9.589	252.9	......	25.94
			156.1	9.115	219.48	......	23.66
			218.1	8.431	143.95	......	16.752
			18.00	9.990	148.10	......	14.603
May 25......	II	30.040	18.00	30.00	259.0	......	8.503
			99.95	28.80	442.4	......	15.109
			156.2	27.37	382.7	......	13.738
			217.9	25.33	249.96	......	9.684
			156.2	27.37	382.5	......	13.730
			99.95	28.80	442.6	......	15.116
			18.00	30.00	259.3	......	8.515
May 26......	II	30.00	18.00	29.96	259.5	......	8.532
			99.83	28.76	442.2	......	15.123
			156.2	27.33	382.7	......	13.755
			217.6	25.30	250.7	......	9.719
			156.4	27.33	381.1	......	13.700
			99.75	28.76	442.6	......	15.136
			18.00	29.96	259.6	......	8.536
May 12......	II	101.67	18.00	101.53	477.9	......	4.636
			99.95	97.47	814.2	......	8.217
			218.0	85.70	458.2	......	5.246

TABLE 33.—*The conductivity data*—Continued.

ACETIC ACID.

Date.	Cell No.	Concentration at 4°.	Temperature, $t°$.	Concentration at $t°$.	Conductance $\times 10^6$.	Conductance capacity.	Equivalent conductance.
1	2	3	4	5	6	7	6
May 13......	II	101.67	18.00	101.53	478.5	......	4.642
			99.98	97.46	815.6	......	8.231
			156.0	92.65	704.2	......	7.468
			217.9	85.71	457.3	......	5.236
			156.1	92.65	703.7	......	7.462
			100.02	97.46	813.2	......	8.207
			18.00	101.53	478.0	......	4.638
May 16......	....	101.67	18.00	101.53	478.3	......	4.641
			30.00	101.24	572.0	......	5.565
			99.56	97.50	815.5	......	8.228
			101.02	97.39	815.0	......	8.231
			98.02	97.61	815.7	......	8.221
			155.8	92.67	705.0	......	7.475
			217.7	85.74	459.4	......	5.257
			99.67	97.49	814.8	......	8.221
			18.00	101.53	478.3	......	4.641

53. SUMMARY OF THE EQUIVALENT-CONDUCTANCE VALUES.

The separate conductance values given in table 33 were all corrected so as to correspond to the uniform temperatures of 18°, 100°, 156°, and 218° by means of temperature-coefficients obtained by plotting those values. In the case of acetic acid, since the equivalent conductance varies rapidly with the concentration, the preceding values were also corrected so as to eliminate the small variations in concentration in the different experiments. This was done with the help of the equation $\Lambda^2 C =$ const., the substantial validity of which will be shown subsequently. The so-corrected equivalent conductances are summarized in table 34. The concentration is expressed in milli-equivalents (referred to oxygen as 16.00) per liter at 4°. In the columns headed "Initial" are given the equivalent conductances obtained from the measurement at the temperature in question before going to the higher temperatures; while in the columns headed "Final" are given the equivalent conductances obtained after returning to the temperature in question from a higher one. The means are based upon both the initial and final values in cases where there was no systematic difference between them; otherwise upon the initial values alone: in which of these ways the mean value was obtained in each separate case, is indicated in the table by its position. From a comparison of the separate initial values at any temperature and concentration the degree of agreement of the determinations made at different times, and often with different solutions, may be seen. A comparison of the initial and final values in the separate experiments shows the contamination that resulted from the heating.

TABLE 34.—*Equivalent conductance at round temperatures.*

Date.	Concentration at 4°.	18°		100°		156°		218°.
		Initial.	Final.	Initial.	Final.	Initial.	Final.	
SODIUM CHLORIDE.								
1904								
Jan. 4.....	0.5003	107.34	107.30	355.7	356.1	546.6	546.7	742.6
Jan. 5.....	0.5003	107.65	113.10	356.2	369.8	*†550.4	565.0	*†752.0
Jan. 8.....	0.5002	107.61	108.17	355.4	357.1	545.8	546.4	739.4
Jan. 9.....	0.5002	*‡107.46	......	......	......	......	......	737.3
Mean ..	0.5002	107.53	......	355.8	......	546.2	......	739.8
1903								
Nov. 28...	2.0009	105.31	......	......	......	......	......	731.3
Dec. 17...	2.0009	105.66	106.05	349.5	351.1	536.0	537.0	725.4
Dec. 18...	2.0009	105.41	106.43	349.7	352.0	536.4	538.9	727.9
Mean ..	2.0009	105.46	......	349.6	......	536.2	......	728.2
Nov. 17...	10.013	101.88	*102.47	335.9	336.4	512.7	513.1	688.7
Nov. 19...	10.013	101.77	......	335.4	......	......	......	......
Nov. 20...	10.013	101.81	......	......	......	......	......	......
Nov. 23...	10.013	101.89	102.11	336.1	......	*516.6	512.7	688.8
Jan. 20...	10.009	102.09	102.03	335.6	336.4	512.1	511.9	688.2
Mean ..	10.012	101.94		336.0		512.5		688.6
HYDROCHLORIC ACID.								
1904								
Feb. 10..	0.4991	375.4	......	836.0	......	1,064.3	......	......
Feb. 12..	0.4996	375.7	374.6	834.6	834.1	*§1,056.7	1,068.4	*§1,234.6
Feb. 13..	"	375.0	......	......	......	......	......	......
Feb. 15..	"	375.0	......	......	......	......	......	......
Mar. 15..	0.4442	373.8	373.0	......	......	......	......	1,241.2
Mar. 16..	‖0.4992	374.1	374.1	832.5	836.0	1,059.7	1,063.2	1,237.8
Apr. 8..	0.4977	375.8	276.1	837.7	839.1	1,068.4	1,070.1	1,246.4
Apr. 9..	"	375.9	376.1	837.6	838.2	1,067.2	1,069.1	1,247.0
Apr. 15..	0.4995	375.9	......	836.2	......	......	......	......
Apr. 16..	0.4995	375.6	......	837.0	......	......	......	1,244.3
Mean .	0.499	375.2	......	835.9	......	1,064.9	......	1,243.3
Feb. 16..	1.9997	373.8	374.0	827.4	827.8	1,048.5	1,051.7	1,224.2
Feb. 17..	"	373.5	373.0	826.4	826.1	1,048.4	1,048.8	1,215.4
Feb. 18..	"	373.5	373.8	......	......	......	......	1,220.3
Mean .	2.000	373.6		826.9		1,049.3		1,219.6
Feb. 20..	9.994	368.2	367.8	808.3	808.7	1,018.5	1,019.5	1,172.0
Feb. 23..	"	368.7	367.2	808.9	808.1	1,019.2	1,016.6	1,176.5
Feb. 24..	"	368.3	368.2	......	......	......	......	1,173.2
Mean .	9.994	368.1		808.5		1,018.5		1,173.9
Mar. 18..	100.66	350.4	350.8	755.6	756.7	933.6	934.3	1,041.3
Mar. 21..	"	350.3	350.8	755.2	755.8	933.5	932.8	1,038.8
Mean. .	100.66	350.6		755.8		933.6		1,040.1

*Data indicated by stars are not included in the mean, on account of their wide deviation from the other values or for some known cause of error stated in the foot notes.

†It is evident from the disagreement of the initial and final values that in this experiment contamination occurred at the higher temperatures.

‡The reading in this case was not of the usual accuracy.

§As the readings were not constant, this value was omitted in computing the mean.

‖The water used in preparing this solution was unusually good, having a specific conductance of only 0.5×10^{-6}.

TABLE 34.—*Equivalent conductance at round temperatures*—Continued.

Date.	Concentration at 4°.	18°		100°		156°		218°.
		Initial.	Final.	Initial.	Final.	Initial.	Final.	
SODIUM ACETATE.								
1904								
Apr. 23...	0.5008	75.82	74.83	274.3	272.0	440.7	434.5	623.8
Apr. 26...	0.4988	76.28	75.17	275.9	272.9	441.4	436.6	629.3
Apr. 27...	0.5015	75.80	75.09	274.1	271.8	438.8	434.1	627.4
Mean ..	0.500	75.97	75.03	274.8	272.2	440.3	435.0	626.8
Apr. 12...	1.9903	*73.77	74.16	267.2	266.7	423.7	422.8	......
Apr. 20...	1.9980	74.57	74.30	268.2	267.3	426.6	425.6	602.3
Apr. 21...	1.9980	74.55	74.30	268.0	267.4	425.9	425.1	600.9
July 14...	1.9985	74.52	74.24	......	......	427.3	......	601.4
Mean ..	1.996	74.55	74.28	267.8	267.1	425.9	424.5	601.5
Mar. 24...	10.002	70.98	70.95	253.6	253.5	399.3	398.8	......
Mar. 25...	10.002	70.96	71.06	253.1	253.6	398.4	397.9	......
June 10...	10.000	71.14	71.18	254.1	253.8	401.2	400.4	......
June 27...	9.992	*70.07	71.40	......	......	394.8	......	551.6
July 5...	9.984	71.23	71.21	......	......	402.1	......	*557.9
July 6...	10.006	71.33	71.34	......	......	398.3	......	551.5
July 7...	10.018	71.23	71.39	......	......	398.6	......	551.3
July 11...	10.001	71.40	71.49	......	......	398.9	......	552.9
Mean ..	10.00	71.22		253.6		399.1		551.8
June 16...	76.06	63.59	......	222.68	......	345.2	......	464.3
June 23...	76.22	63.75	63.68	222.89	222.58	......	344.9	463.6
Mean ..	76.14	63.67		222.72		345.1		464.0
June 14...	95.55	62.28	*62.43	217.82	*218.09	337.0	*338.8	450.7
ACETIC ACID.								
1904								
May 20...	10	14.585	14.564	25.92	25.94	23.68	23.68	16.730
May 24...	"	14.589	14.579	25.96	......	*†23.79	......	*†17.013
June 2...	"	14.583	14.603	25.94	......	23.67	......	16.768
Mean ..	10	14.586	14.581	25.94	......	23.68	......	16.749
May 25...	30	8.512	8.524	15.124	15.131	13.761	13.753	9.685
May 26...	"	8.532	8.536	15.123	15.138	13.764	13.718	9.683
Mean ..	30	8.522	8.530	15.124	......	13.763	......	9.684
May 12...	100	4.673	......	8.283	......	......	......	5.288
May 13...	"	4.679	......	8.297	8.273	7.528	7.524	5.271
May 16...	"	4.678	4.678	8.294	8.287	7.530	......	5.286
Mean ..	100	4.677	......	8.291	......	7.529	......	5.282

*Omitted in computing the mean.

†Omitted in computing the mean since the readings were uncertain, owing to the fact that a relatively high vacuum was produced in this case, which permitted the formation of bubbles on the electrode.

In connection with these results, attention may be called to the degree of agreement of the "initial" and "final" values, which gives a measure of the change in concentration resulting from the heatings. In the cases of the 0.1 and 0.01 normal solutions of sodium chloride, hydrochloric acid, acetic acid, and sodium acetate the differences between these two sets of values at all temperatures are scarcely greater than the possible experimental errors of the separate determinations. Remarkably enough, the same is true, in the case of the hydrochloric acid, of the still more dilute solutions, 0.002 and 0.0005 normal. In the case of sodium chloride at these two concentrations the final values at 18° are as a rule somewhat larger than the initial values, but on an average only by 0.5 per cent. In the case of sodium acetate, on the contrary, the final values are smaller by 0.3 to 0.4 per cent for the 0.002 normal solution and by 1.0 to 1.5 per cent for the 0.0005 normal solution.

Table 35 contains a summary of the mean values of the equivalent conductances given in table 34, after correcting them upon the basis described in section 16, Part II, for the change in conductance caused by the heating (only, however, in cases where the initial and final values at 18° differed by more than 0.25 per cent). The acetic acid values given under the heading "corrected" were obtained by decreasing the "uncorrected" values by a fractional amount equal to the ratio of the actual conductance in the bomb of the water (section 51) to that of the solution in question. The values of the concentrations here given are those at the temperatures of the measurements. They were obtained by dividing the concentration at 4° by the appropriate specific-volume-ratio.

TABLE 35.—*Mean values of the equivalent conductance.*

Temperature.	Concentration.	Sodium chloride.	Hydrochloric acid.	Sodium acetate.	Acetic acid.	
					Uncorrected.	Corrected.
18°	0.500	107.53	375.2	75.97	......	......
	1.998	105.46	373.6	74.55	......	......
	9.99	101.94	368.1	71.22	14.59	14.50
	30.0	......	......	......	8.52	8.49
	75.9	......	......	63.67	......	......
	99.9	......	350.6	......	4.68	4.67
100°	0.479	355.8	836	274.8	......	......
	1.917	349.4	827	267.8	......	......
	9.59	336.0	808	253.6	25.94	25.64
	28.8	......	......	......	15.12	15.01
	72.9	......	......	222.7	......	......
	95.9	......	756	......	8.29	8.26
156°	0.456	546	1,065	440.3	......	......
	1.82	535	1,049	425.9	......	......
	9.11	513	1,018	399.1	23.68	23.14
	27.3	......	......	......	13.76	13.57
	69.2	......	......	345.1	......	......
	91.1	......	934	......	7.53	7.47
218°	0.422	740	1,243	631	......	......
	1.69	725	1,220	603	......	......
	8.43	689	1,174	552	16.75	15.93
	25.3	......	......	......	9.68	9.40
	64.1	......	......	464	......	......
	84.3	......	1,040	......	5.28	5.20

54. EQUIVALENT-CONDUCTANCE VALUES AT ROUND CONCENTRATIONS.

In order to show more clearly the change of conductance with the temperature the values in table 35 have been reduced so as to correspond to the same concentration at all temperatures. This has been done by graphic interpolation with the help of the approximately linear function $\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + K(C\Lambda)^{\frac{1}{2}}$ in the cases of sodium chloride, hydrochloric acid and sodium acetate; and with the help of the function $\Lambda = K(\frac{1}{C})^{\frac{1}{2}}$, also approximately linear, in the case of acetic acid. Values extrapolated for any considerable interval are indicated by inclosure in parentheses. The limiting values for zero concentration (Λ_0) were derived for hydrochloric acid and sodium acetate by determining graphically what function of the exponential form $\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + K(C\Lambda)^{n-1}$ would best express the results at 0.5, 2, 10 and 100 (or 75 or 85) milli-normal and extrapolating for zero concentration (see section 42, Part IV). For sodium acetate the conductance values at 156° and 218° were first corrected for the hydrolysis of the salt in the way to be described in section 58, before making this extrapolation. The corrected values are given in the table below the uncorrected ones. At 18° and 100° the hydrolysis is inappreciable. For acetic acid the Λ_0 values were calculated from those for the other three substances by the law of the independent migration of the ions.

Table 36 contains the results of these computations. The concentrations, as usual in this article, are expressed in milli-equivalents per liter (referred to oxygen as 16.00) and the temperatures are on the hydrogen gas scale.

TABLE 36.—*Equivalent conductance at round concentrations.*

Substance.	Concentration.	18°.	100°.	156°.	218°.
Sodium Chloride..........	0.5	107.53	355.5	545	738
	2.0	105.46	349.0	534	722
	10.0	101.94	335.5	511	684
Hydrochloric Acid........	0	379	850	1,085	1,265
	0.5	375.2	835	1,064	1,241
	2.0	373.6	826	1,048	1,217
	10.0	368.1	807	1,016	1,168
	80.0	353.0	762	946	1,044
	100.0	350.6	754	929	1,006
Sodium Acetate (uncorrected for hydrolysis)	0	78.1	285	.....	....
	0.5	75.97	274.6	439.5	628
	2.0	74.55	267.6	424.5	598
	10.0	71.22	253.3	397.0	546
	80.0	63.4	221.0	340.0	453

TABLE 36.—*Equivalent conductance at round concentrations*—Continued.

Substance.	Concentration.	18°.	100°.	156°.	218°.
Sodium Acetate (corrected for hydrolysis)	0	......	......	450	660
	2.0	......	......	421	578
	10.0	......	......	396	542
	80.0	......	......	340	452
Acetic Acid (uncorrected for conductance of water).	10	14.59	25.40	22.65	15.43
	30	8.52	14.80	13.13	8.90
	80	5.23	9.10	8.07	5.42
	100	4.68	8.13	......	......
Acetic Acid (corrected for conductance of water).	0	347	773	980	1,165
	10	14.50	25.10	22.15	14.70
	30	8.50	14.70	12.95	8.65
	80	5.22	9.05	8.00	5.34
	100	4.67	8.10	......	......

The results with sodium chloride were in an earlier part of this publication combined with the other results obtained with this substance in this laboratory and were discussed in connection with them (see section 16, Part II). The results with the other substances will alone be considered in the following pages. In the case of the acetic acid we shall employ the values corrected for the conductance of the water.

It is of interest to compare these results with those of previous investigators in the few cases in which duplicate data already exist. In table 37 such data are placed side by side.

TABLE 37.—*Comparison of the values of the equivalent conductance at 18° obtained by different investigators.*

Concentration.	HYDROCHLORIC ACID.			SODIUM ACETATE.		ACETIC ACID.	
	Noyes and Cooper.	Kohlrausch.*	Goodwin and Haskell.†	Noyes and Cooper.	Kohlrausch.*	Noyes and Cooper.	Kohlrausch.*
0.5	375.2	......	375.4	76.0	75.8	......	......
2.0	373.6	376	375.0	74.5	74.3	......	......
10.0	368.1	370	369.3	71.2	70.2	14.50	14.3
100.0	350.7	351	351.4	......	......	4.67	4.60

*Kohlrausch and Holborn, Leitvermögen der Elektrolyte, 159-160, (1898).

†Proc. Am. Acad., **40**, 409, 415 (1904); Phys. Rev., **19**, 383, 386 (1904). The values here given, like our own, are uncorrected for the influence of the water.

Our results with hydrochloric acid at 18° agree on an average within 0.25 per cent with those determined with great care by Goodwin and Haskell. This is also true of the values for this acid extrapolated for zero concentration, which are 379 and 380 respectively. Our values for sodium acetate in 0.01 normal and for acetic acid in 0.1 normal solution differ, however, from the early ones of Kohlrausch by 1.4 and 1.5 per cent respectively.

55. CHANGE OF THE EQUIVALENT CONDUCTANCE WITH THE CONCENTRATION AND TEMPERATURE.

The change of the conductance with the concentration may be first discussed. In the case of the sodium acetate values uncorrected for hydrolysis there is, owing to this phenomenon, an abnormally large increase between the highest and lowest concentrations, especially at the higher temperatures. Moreover, it is not probable that the values corrected for hydrolysis are as accurate as those for unhydrolyzed salts. This makes it scarcely worth while to investigate fully the form of function applicable to the change of conductivity with the concentration in the case of this salt. Of much interest, however, is such a study in the case of hydrochloric acid, especially with reference to the conformity of its behavior to that of the neutral salts. We have therefore tested the applicability to the data of the three functions $\Lambda_0 - \Lambda = KC^{\frac{1}{2}}$ (Kohlrausch), $\Lambda_0 - \Lambda = KC^{\frac{1}{2}}\Lambda^{\frac{1}{2}}$ (Barmwater), and $\Lambda_0 - \Lambda = K^{\frac{3}{2}}C^{\frac{1}{2}}$ (van't Hoff), by plotting the values of Λ along one co-ordinate axis and those of $C^{\frac{1}{2}}$, $\Lambda^{\frac{1}{2}}C^{\frac{1}{2}}$, or $\Lambda^{\frac{3}{2}}C^{\frac{1}{2}}$ along the other axis, drawing the best representative straight line through the points in such a way as to make the percentage deviations of the two conductivity values for the more concentrated solutions (10 and 100 or 10 and 85 milli-normal) and also of those for the more dilute solutions opposite and equal, and reading off the deviations of the separate points from the line. These deviations, expressed as percentages of the conductance values, are given in table 38.

TABLE 38.—*Deviation of the observed conductance values for hydrochloric acid from those calculated by various empirical formulas.*

Temperature.	Concentration.	Equivalent conductance.	Percentage deviation of observed from calculated conductance values.		
			$C^{1/2}$	$\Lambda^{1/2}C^{1/2}$	$\Lambda^{3/2}C^{1/2}$
18°	0.5	375.2	−0.19	−0.20	−0.08
	2.0	373.6	+0.17	+0.19	+0.06
	9.99	368.1	+0.22	+0.27	−0.02
	99.9	350.6	−0.24	−0.27	+0.01
	Mean.	......	0.21	0.24	0.04
100°	0.479	836	−0.05	−0.08	+0.11
	1.917	827	+0.05	+0.06	−0.13
	9.59	808	+0.07	+0.12	−0.22
	95.9	756	−0.07	−0.13	+0.21
	Mean.	......	0.06	0.10	0.17
156°	0.456	1,065	+0.01	−0.05	+0.18
	1.82	1,049	−0.01	+0.02	−0.18
	9.11	1,018	0.00	+0.08	−0.40
	91.1	934	0.00	−0.09	+0.42
	Mean.	......	0.01	0.06	0.30
218°	0.421	1,243	−0.09	−0.09	+0.21
	1.69	1,220	0.00	+0.10	−0.28
	8.43	1,174	+0.10	+0.22	−0.74
	84.3	1,040	−0.12	−0.33	+0.68
	Mean.	......	0.06	0.18	0.47

It will be seen from the table that as in the case of the salts previously investigated, the cube-root function of Kohlrausch expresses the results almost perfectly at the three higher temperatures, but that at 18° the deviations reach 0.25 per cent. That of Barmwater is nearly, but not quite, as satisfactory. On the other hand, the function of van't Hoff well represents the data at 18°, but does so less and less perfectly the higher the temperature, so that at 218° the deviations reach 0.7 per cent.

We have also determined graphically, by plotting $1/\Lambda$ against $(\Lambda C)^{n-1}$ (see section 17, Part II), what value of the exponent n in the function $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$ best expresses the results at the different temperatures both for hydrochloric acid and sodium acetate (unhydrolyzed values). The results are given in table 39.

TABLE 39.—*Values of the exponent n in the function* $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$

Substance.	18°.	100°.	156°.	218°.
HCl..........	1.45	1.38	1.40	1.47
$NaC_2H_3O_2$....	1.45	1.45	1.42	1.36

The effect of temperature is mainly of interest when considered with reference to the conductivity values extrapolated for zero concentration; for this effect then consists solely in a change in the migration velocity of the ions, while at higher concentrations upon this the change in ionization is superposed. To show the character of this effect, we have calculated the mean absolute temperature-coefficient of the conductivity at zero concentration $\Delta\Lambda_0/\Delta t$ between 18° and 100°, 100° and 156°, and 156° and 218°. These coefficients are given in the following table, together with the value of the equivalent conductance at 18°. The coefficients for sodium acetate are based on the conductance values corrected for hydrolysis.

TABLE 40.—*Mean temperature-coefficients of the equivalent conductance at zero concentration.*

Substance.	Conductance at 18°.	Temperature-coefficient.		
		18°–100°.	100°–156°.	156°–218°
NaCl..........	109	3.09	3.44	3.31
$NaC_2H_3O_2$...	78.1	2.53	2.95	3.40
HCl............	379	5.76	4.20	2.90

It is evident from the preceding table that the temperature-coefficient of sodium acetate, like that of the other uni-univalent salts discussed in Parts II and IV first increases rapidly,* attains a maximum, and then somewhat decreases. Hydrochloric acid, on the contrary, exhibits a constantly decreasing temperature-coefficient.*

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*According to Arrhenius (Ztschr. phys. Chem., **4**, 99, 1889) its absolute temperature-coefficient for the interval 18-52° is 2.08, thus much smaller than that from 18° to 100°.

It is also worthy of note that the migration velocities of the ions of these three substances differ by a less percentage amount the higher the temperature. Thus the ratio of the equivalent conductance of sodium acetate and of hydrochloric acid at zero concentration to that of potassium chloride has the following values at the various temperatures:

	18°	100°	156°	218°
$NaC_2H_3O_2$: KCl	0.60	0.69	0.72	0.80
HCl : KCl	2.91	2.05	1.73	1.53

The effect of temperature on the conductivity at the higher concentrations does not require special discussion, since the phenomenon is better analyzed through the consideration, presented in the following section, of the relation of ionization to temperature. It is, however, of some interest to note that acetic acid, owing to the decrease in its ionization overcompensating the increase in the migration velocity of its ions, has a maximum value of the equivalent conductance at some temperature between 18° and 156°.

56. IONIZATION-VALUES AND THEIR CHANGE WITH THE CONCENTRATION AND TEMPERATURE.

Table 41 shows the percentage degree of ionization of the various substances. These values were obtained merely by dividing the conductances at the different concentrations by the conductance at zero concentration, all of which are given in table 36. The values corrected for hydrolysis were used in the case of sodium acetate, and those corrected for the conductance of the water in the case of acetic acid.

TABLE 41.—*Percentage ionization.*

Substance.	Concentration.	18°.	100°.	156°.	218°.
Hydrochloric Acid.	0	100.0	100.0	100.0	100.0
	0.5	99.0	98.2	98.0	98.2
	2	98.5	97.2	96.5	96.0
	10	97.1	95.0	93.6	92.2
	80	93.2	89.7	87.2	82.5
	100	92.6	88.7	85.6	79.5
Sodium Acetate.	0.5	97.2	96.4	......	......
	2	95.3	93.8	93.7	87.2
	10	91.2	88.8	88.0	82.2
	80	81.1	77.6	75.6	68.5
Acetic Acid.	10	4.17	3.24	2.26	1.26
	30	2.45	1.90	1.32	0.743
	80	1.50	1.17	0.815	0.458
	100	1.34	1.05	......	......

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*Its value for the interval 10-30° is 6.30 (computed from the data of Noyes and Sammet [Ztschr. phys. Chem., **43**, 70, 1903] and our value of Λ_0 at 18°).

The discussion, given in section 55, of the change of conductivity of hydrochloric acid with the concentration is substantially also a discussion of the change of ionization; for the three functions there considered, provided each be assumed to hold down to zero concentration and therefore to give the true value of Λ_0, may be written in the forms:

$$1-\gamma=KC^{\frac{1}{3}};\ 1-\gamma=K(C\gamma)^{\frac{1}{2}} \text{ and } C(1-\gamma)=K(C\gamma)^{\frac{3}{2}}$$

The conductivity functions corresponding to the first two of these have been shown to express the results fairly satisfactorily in all cases; but this is not true, especially at the higher temperatures, of the function corresponding to the last of these expressions. It was in fact shown that the exponent in the expression corresponding to the general exponential function $C(1-\gamma)=K(C\gamma)^n$ has both for hydrochloric acid and sodium acetate values differing from 1.5 and varying somewhat with the temperature (see table 39).

The question of the applicability of the mass-action law to the results with acetic acid at the higher temperatures is of considerable interest. The values of its ionization-constant (multiplied by 10^6) calculated from the data of table 41 by the equation $K=C\gamma^2/(1-\gamma)$ are given in table 42, the concentration used in the calculation and given in the table being expressed in equivalents (not milli-equivalents) per liter.

TABLE 42.—*Ionization-constants* (10^6K) *for acetic acid.*

Concentration.	18°.	100°.	156°.	218°.
0.01	18.15	10.85	5.23	1.61
0.03	18.46	11.04	5.30	1.67
0.08	.....	.....	5.36	1.69
0.10	18.20	11.14	....	....

It is evident from these results that the mass-action law holds true, at least approximately, for this acid at 218°, just as it does at 18°. The values given in the last rows — those for the more concentrated solutions — are doubtless the best values of the constant.

It will be seen from table 41 that the ionization of all these substances decreases steadily with rising temperature. In 0.1 normal solution the decrease between 18° and 218° is nearly the same (9 to 11 per cent) for the first three substances, and consequently their relative degrees of ionization are not much different at the higher and lower temperatures. The decrease in the case of acetic acid is very great, the ionization at 218° being only about one-third of that at 18°; moreover, the decrease is especially rapid above 100°. Correspondingly, its ionization-constant (given in table 42) has decreased at 100° to about 0.6 and at 218° to about 0.1 of its value at 18°.

57. CONDUCTIVITY DATA FOR MIXTURES OF SODIUM ACETATE AND ACETIC ACID.

Table 43 gives the results that were obtained with the mixtures of sodium acetate and acetic acid. The values of the conductance are the measured values in reciprocal ohms, multiplied by 10^6 and corrected for the instrumental errors and the lead resistance. The values of the specific conductance were calculated from these by applying the water-correction and multiplying by the conductance-capacity.

It will be seen that with the 2 and 76 milli-normal salt solutions the initial and final values of the specific conductance agree in every case within about 0.1 per cent, and that with the 10 milli-normal solution the two values differ on an average by only 0.2 per cent. This makes it improbable that the results are affected by an error arising from contamination or adsorption.

58. HYDROLYSIS OF SODIUM ACETATE AND IONIZATION OF WATER.

The increase in conductance due to hydrolysis of the salt can be derived from the data of table 43 and those obtained with sodium acetate alone (table 35). It is first necessary to subtract from the former values the conductance which the acetic acid itself possesses in the mixture. This can be determined by the application of the mass-action law, which has already been shown to apply to acetic acid at all the temperatures. According to this law $\frac{C_{\mathrm{H}} \times C_{\mathrm{Ac}}}{C_{\mathrm{HAc}}} = K$. Now C_{Ac} is substantially equal to the concentration of the ionized sodium acetate in the solution, which is readily calculated by multiplying its concentration (C_s) by the corresponding ionization value (γ_s) taken from table 41. The ionization of the acetic acid $\frac{C_{\mathrm{H}}}{C_{\mathrm{HAc}}}$ is then found by dividing its ionization-constant by this product, and its specific conductance ($\underline{\mathrm{L}}_{\mathrm{A}}$) is equal to the product of this ionization value by the concentration of the acid (C_{A}) and by its equivalent conductance when completely ionized ($\Lambda_{0\mathrm{A}}$), i. e., $\underline{\mathrm{L}}_{\mathrm{A}} = \frac{K}{C_s \gamma_s} \cdot C_{\mathrm{A}} \Lambda_{0\mathrm{A}}$. The specific conductance of the acid is then subtracted from the specific conductance of the mixed solution, whereby the specific conductance of the unhydrolyzed salt is obtained. It is assumed hereby that the acetic acid has been added in sufficient amount to reduce the hydrolysis to a value not differing appreciably from zero; that this was the case was proved experimentally by the addition of varying amounts of acetic acid, and it will also be shown theoretically that even the smallest addition made in our experiments must have sufficed.

The data and results of these calculations are given in table 44, which is more fully explained on page 146.

TABLE 43.—*The conductivity data for mixtures of sodium acetate and acetic acid.*

Date.	Cell No.	Concentration at 4°.		Temperature.	Conductance × 10⁶.	Specific conductance × 10⁶.
		Sodium acetate.	Acetic acid.			
1904						
July 15...	III	1.9925	1.594	18.00	1,039.4	153.34
				156.5	5,252	772.9
				217.7	6,660	978.7
				18.00	1,039.9	152.56
July 18...	III	2.0043	0.874	18.00	1,027.1	151.55
				156.3	5,267	775.2
				18.00	1,026.4	150.56
July 19...	III	2.0071	0.456	18.00	1,019.6	150.41
				156.3	5,268	775.3
				217.4	6,712	986.5
				18.00	1,020.7	149.71
July 20...	III	2.0021	0.464	18.00	1,017.3	150.07
				155.8	5,245	771.9
				217.2	6,691	983.3
				18.00	1,017.9	149.30
June 7...	II	9.967	5.53	18.00	723.4	711.7
				217.7	4,706	4,610
June 8...	II	10.052	1.951	18.00	726.9	715.1
				217.9	4,755	4,658
June 9...	II	10.003	3.61	18.00	724.7	713.0
				218.4	4,738	4,642
June 28...	III	10.002	3.50	18.00	4,823	714.9
				157.2	24,673	3,650
				217.9	31,290	4,624
				18.00	4,839	716.4
June 29...	III	10.023	2.739	18.00	4,819	714.4
				155.8	24,588	3,637
				217.6	30,890	4,565
				18.00	4,839	716.4
July 7...	III	10.016	2.225	18.00	4,827	715.5
				155.9	24,594	3,638
				217.8	31,180	4,608
				18.00	4,828	714.8
July 8...	III	10.036	2.162	18.00	4,833	716.4
				217.9	31,350	4,633
				18.00	4,843	717.0
July 9...	III	10.015	2.228	18.00	4,819	714.4
				217.9	31,240	4,617
				18.00	4,827	714.7
June 17..	II	76.18	20.54	18.00	4,912	4,837
				156.3	24,402	23,998
				218.3	30,320	29,736
				18.00	4,914	4,838
June 20...	II	76.06	20.67	18.00	4,888	4,814
				156.0	24,079	23,654
				217.7	30,100	29,526
				18.00	4,876	4,801
June 24...	II	76.08	20.67	18.00	4,911	4,836
				100.08	16,532	16,258
				156.3	24,361	23,936
				218.0	30,270	29,686
				18.00	4,912	4,836

TABLE 44.—*Specific conductance of the constituents of the sodium acetate solutions.*

Date.	Temperature, $t°$.	Concentration at $t°$.		Specific conductance × 10^6.				Difference.	Percentage difference.
		Salt.	Acid.	Mixture.	Acid in mixture.	Salt in mixture.	Salt in water alone.		
1	2	3	4	5	6	7	6	9	10
July 15.	18	1.990	1.592	153.34	5.31	148.03	148.35	0.32	
July 18.	18	2.002	0.873	151.55	2.90	148.65	149.22	0.57	
July 19.	18	2.004	0.455	150.41	1.51	148.90	149.43	0.53	
July 20.	18	1.999	0.464	150.07	1.54	148.53	149.05	0.52	
Mean .	....	......	......	......	......	......	......	0.49	0.33
June 7.	18	9.953	5.52	711.7	3.9	707.8	708.9	1.1	
June 8.	18	10.038	1.949	715.1	1.4	713.7	714.9	1.2	
June 9.	18	9.989	3.60	713.0	2.5	710.5	711.5	1.0	
June 28.	18	9.989	3.49	714.9	2.4	712.5	711.5	—1.0	
June 29.	18	10.010	2.735	714.4	1.9	712.5	712.9	0.4	
July 7.	18	10.002	2.222	715.5	1.5	714.0	712.3	—1.7	
July 8.	18	10.023	2.159	716.4	1.5	714.9	713.8	—1.1	
July 9.	18	10.001	2.225	714.4	1.5	712.9	712.2	—0.7	
Mean .	....	......	......	......	......	......	......	—0.1	0.0
June 17.	18	76.08	20.51	4837	2	4835	4844	9	
June 20.	18	*75.95	20.64	4814	2	*4812	4836	*24	
June 24.	18	75.98	20.64	4836	2	4834	4838	4	
Mean .	....	......	......	......	......	......	......	6	0.1
July 15.	156	1.815	1.452	770.8	4.6	766.2	773.0	6.8	
July 18.	156	1.826	0.796	773.9	2.5	771.4	777.7	6.3	
July 19.	156	1.829	0.415	774.0	1.3	772.7	779.0	6.3	
July 20.	156	1.824	0.423	772.7	1.3	771.4	776.8	5.4	
Mean .	....	1.824	......	......	......	770.4	......	6.2	0.80
June 28.	156	9.113	3.19	3626	2	3624	3637	15	
June 29.	156	9.132	2.495	3641	2	3639	3645	6	
July 7.	156	9.125	2.027	3640	1	3639	3642	3	
Mean .	....	......	......	......	......	......	......	8	0.22
June 17.	156	69.41	18.72	23962	2	23960	23953	—7	
June 20.	156	*69.30	18.83	23654	2	*23652	23915	*263	
June 24.	156	69.32	18.83	23900	2	23898	23922	24	
Mean .	....	......	......	......	......	......	......	8	0.05
July 15.	218	1.680	1.344	979.8	1.8	978.0	1013.1	35.1	
July 19.	218	1.692	0.384	988.5	0.5	988.0	1020.3	32.3	
July 20.	218	1.688	0.391	986.3	0.5	986.0	1017.9	31.9	
Mean .	....	1.687	......	......	......	984.0	......	33.1	3.25
June 7,	218	8.402	4.66	4615	1	4614	4638	24	
June 8.	218	8.473	1.645	4660	0	4660	4677	17	
June 9.	218	8.432	3.04	4635	1	4634	4654	20	
June 28.	218	8.431	2.95	4626	1	4625	4654	29	
June 29.	218	8.454	2.309	4571	1	4570	4667	97	
July 7.	218	8.443	1.875	4611	1	4610	4661	51	
July 8.	218	8.460	1.823	4635	1	4634	4670	36	
July 9.	218	8.442	1.878	4619	1	4618	4660	42	
Mean .	....	8.442	......	......	......	4621	......	40	0.85
June 17.	218	64.22	17.32	29716	1	29715	29798	83	
June 20.	218	*64.11	17.43	29546	1	*29545	29747	*202	
June 24.	218	64.13	17.42	29686	1	29685	29757	68	
Mean .	....	64.18	......	......	......	29700	......	75	0.25

*Values to which an asterisk is attached were, on account of their large deviation, omitted in computing the mean.

The first column of table 44 contains the date, which correlates the data with those of table 43; and the second column, the temperature. The third and fourth columns give the concentrations in the mixture of the sodium acetate and acetic acid, respectively, found by dividing the concentrations at 4° by the specific-volume ratios. The fifth column contains the specific conductance of the mixture, the values at the two higher temperatures being corrected so as to correspond to the even temperatures, 156° and 218°. In the sixth column is given the specific conductance of the acetic acid in the mixture, calculated as just described. The values in the seventh column, which represent the specific conductance of the unhydrolyzed salt, were obtained by subtracting those in the sixth column from those in the fifth. The numbers in the eighth column show the specific conductance of the salt when present alone in water at the same concentration; they were calculated by multiplying the equivalent conductances given in table 35 by the concentration of the salt in the mixture in question. The ninth column contains the differences between the values of the two preceding columns and shows the decrease in specific conductance produced by the addition of the acetic acid. The last column shows the percentage value of the decrease, referred to the specific conductance of the unhydrolyzed salt given in the seventh column.

In connection with these results it may be first stated that the values of the equivalent conductance for unhydrolyzed sodium acetate at 156° and 218° already included in table 36 were computed by dividing the mean specific conductance of the "salt in mixture," given in column 7, of table 44 by the mean concentration given in column 3, and then interpolating the values for round concentrations and calculating those for zero concentration in the way described in the statement preceding table 36.

It will be seen from the values for the percentage decrease of the specific conductance given in the last column of the table that only at 218°, and perhaps in the most dilute solution at 156°, are the values greater than the probable experimental error. We shall therefore calculate the hydrolysis corresponding only to these values. In order to make this calculation, it is necessary to know, in addition to the foregoing data, the specific conductance of sodium hydroxide. Values for the equivalent conductance of this substance have recently been obtained by Noyes and Kato in this laboratory, and are presented in table 58, section 67, Part VI. From these the specific conductance at any concentration can be readily calculated. The values for sodium acetate at various concentrations are given in the foregoing table in the column headed "salt in mixture." The difference in the specific conductances of these two substances at any concentration represents the decrease of specific conductance which would be observed if the total quantity of sodium hydroxide in a solution of it were transformed into sodium acetate. Assuming now for the moment that the degree of ionization of each of the two substances in a mixture of them is substantially the same as if it were present alone at the same total concentration, it is evident that the ratio of the observed decrease in specific conductance produced by the addition of the acetic acid to this calculated difference in the specific conductances of the two substances is equal to the degree of hydrolysis of the salt or to the proportion of it that exists in the state of hydroxide; provided, of course, the addition of acid has been sufficient to reduce the hydrolysis to appreciably zero. That the actual ionization relations are in fact those just assumed will be evident from the following considerations. Since the hydrolysis is small, the concentration of the sodium acetate will not be greatly changed when the hydroxide is converted to acetate, and, therefore, the new sodium acetate will have a degree of ionization and equivalent conductance substantially equal to that of the main quantity of the salt. Moreover, even though the hydroxide exists in the presence of a much larger proportion of the acetate, its degree of ionization and equivalent conductance will have that value which it would have if it were present alone in water at a concentration approximately equal to the concentration of the acetate, in virtue of the principle that, in a mixture of two largely and nearly equally ionized electrolytes, each has that degree of ionization which it has when present alone at a concentration equal to the sum of the concentrations of the two electrolytes.[*]

The following table contains the results of the calculation of the hydrolysis and also the data upon which it is based. The values given in the third and sixth columns are taken directly from table 44. Those in the fourth were obtained by interpolating graphically the equivalent conductance of sodium hydroxide from the results of Noyes and Kato and multiplying it by the concentration given in the second column.

TABLE 45.—*Hydrolysis of sodium acetate.*

Temperature (t°)	Concentration at t°.	Specific conductance $\times 10^6$.				Percentage hydrolysis.
		Unhydrolyzed acetate.	Sodium hydroxide.	Difference between hydroxide and acetate.	Observed difference between hydrolyzed and unhydrolyzed acetate.	
156	1.824	770.4	1,484	713.6	6.2	0.87
218	1.687	984.0	1,738	754	33.1	4.34
218	8.442	4,621	8,196	3,575	40	1.12
218	64.18	29,700	55,390	25,690	75	0.29

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[*] See Noyes, Congress of Arts and Science, St. Louis Exposition, **4**, 318 (1904); Science, **20**, 577-87 (1904); Technology Quart., **17**, 301 (1904).

It is of interest in the first place to compare the hydrolysis at 156° and 218° with that at 18°. For this purpose we will select the values obtained at a concentration of 1.82 or 1.69 milli-normal; for these are probably the most accurate of our results, since the hydrolysis was largest in these cases. At this concentration the degree of hydrolysis of the sodium acetate is 0.87 per cent at 156° and 4.3 per cent at 218°, while at 18° the value calculated from the ionization constants of water and acetic acid is only 0.07 per cent. The effect of temperature is therefore enormous. This arises in part from the decrease in ionization of the acetic acid, which has been already considered, but in still larger measure from an increase in the ionization of water, as will now be shown.

The mass-action formula applicable to a hydrolysis of this type, where the salt and base can be regarded as equally ionized, and the acid as unionized is $\frac{h^2C}{1-h} = \frac{K_W}{K_A}$ where h is the fraction hydrolyzed, C is the concentration of the salt, and K_W and K_A are the ionization-constants of the water and acid respectively. By means of this the ionization-constant of the water at 218° can be calculated, since the other three quantities involved are known.

This calculation has been made with the help of the hydrolysis values of table 45 and the ionization-constants given in table 42. The data and results of the calculation (with the concentrations expressed in equivalents per liter) are given in table 46. By C_H is to be understood the concentration of the hydrogen (or hydroxide) ions in pure water, the values being equal to the square root of K_W.

TABLE 46.—*Ionization-constants of water.*

t	C	$100\,h$	$10^6 K_A$	$10^{14} K_W$	$10^7 C_H$
18	......	....	....	0.64	0.80
156	0.00182	0.87	5.36	75	8.7
218	0.00169	4.34	1.69	562	24
218	0.00844	1.12	1.69	182	14

It will be seen that the ionization-constant of water is 115 times as great at 156° and 580 times as great at 218° as it is at 18°, for which temperature we have inserted the values derived by Kohlrausch and Heydweiller* from the conductivity of the purest water obtained by them. Correspondingly, the ionization itself or the concentration of the hydrogen and hydroxide ions in it is 11 times as great at 156°, and 24 times as great at 218°, as it is at 18°.

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*Wied. Ann. Phys., 53, 234 (1894). See also Nernst, Theoretische Chemie, 4te Aufl., p. 644.

The disagreement between the two values of the ionization-constant at 218° derived from the hydrolysis data at different concentrations is doubtless due to experimental error in these data, and shows that that error is large. These values of the ionization-constant are therefore to be regarded only as very rough approximations. Far more reliable and accurate values have been since obtained by a similar investigation of the much more hydrolyzed ammonium acetate made in this laboratory by Noyes and Kato and by R. B. Sosman and presented in Parts VI and VII of this publication.

59. SUMMARY.

In this article have been presented the results of conductivity measurements at concentrations varying from 0.0005 to 0.1 normal and at the temperatures 18°, 100°, 156°, and 218° for solutions of hydrochloric acid, sodium chloride, acetic acid, and of sodium acetate alone and in the presence of an excess of acetic acid. The equivalent conductance of these substances at zero concentration was determined by extrapolation or through the law of independent migration-velocity; and the ionization at the various concentrations was calculated. The hydrolysis of sodium acetate at 156° and 218° was also roughly determined from the decrease in conductance produced by adding acetic acid to its solution; and from this hydrolysis and the ionization-constant of acetic acid, the ionization of water itself was estimated.

The equivalent conductances at zero concentration of hydrochloric acid and sodium acetate both approach that of potassium or sodium chloride as the temperature rises, thus again exemplifying the principle that the relative velocities of different ions approach equality with rising temperature.

The ionization (γ) both of hydrochloric acid and of sodium acetate, though the former is several per cent larger, and the latter several per cent smaller, under comparable conditions, than that of the neutral salts of the same type previously investigated (see Parts II and IV), yet varies with the concentration (C) according to the same exponential law, $(C\gamma)^n/C(1-\gamma) = \text{const.}$ where $n = 1.38$ to 1.47, as does that of the other uni-univalent substances. The ionization of both these substances decreases with rising temperature, slowly between 18° and 100°, but more rapidly at the higher temperatures. The ionization of acetic acid also decreases steadily with increasing temperature, its ionization-constants multiplied by 10^6 being 18.2 at 18°, 11.1 at 100°, 5.4 at 156°, and

1.69 at 218°. It conforms fairly well to the mass-action law at all temperatures.

The hydrolysis of sodium acetate proved to be rather small even at 218°, being only about 1 per cent in 0.01 normal solution, and could not therefore be accurately determined. A rough estimate of the ionization-constant of water ($K_W = C_H \times C_{OH}$) based on the hydrolysis data gave at 218° the value 372×10^{-14}, which, when compared with the value at 18° (0.6×10^{-14}), shows the enormous increase produced by temperature.

PART VI.

CONDUCTIVITY AND IONIZATION OF SODIUM HYDROXIDE UP TO 218° AND OF AMMONIUM HYDROXIDE AND CHLORIDE UP TO 156°. HYDROLYSIS OF AMMONIUM ACETATE AND IONIZATION OF WATER AT 100° AND 156°.

BY ARTHUR A. NOYES AND YOGORO KATO.

PART VI.

CONDUCTIVITY AND IONIZATION OF SODIUM HYDROXIDE UP TO 218° AND OF AMMONIUM HYDROXIDE AND CHLORIDE UP TO 156°. HYDROLYSIS OF AMMONIUM ACETATE AND IONIZATION OF WATER AT 100° AND 156°.

60. OUTLINE OF THE INVESTIGATION.

The investigation of Noyes and Cooper (Part V) having shown that the hydrolysis of sodium acetate was not great enough at 100° or 156° to permit of the calculation of the ionization of water, we were led to undertake a similar study at these temperatures of ammonium acetate, a salt of a much weaker base whose hydrolysis would therefore be far more considerable. In this case it would be practicable to reduce the hydrolysis by the addition of an excess both of the acid and of the base, since both are only slightly conducting substances; and there would result an increase (instead of decrease) of conductivity corresponding almost exactly to that of the new quantity of ammonium acetate thereby produced out of the free acid and base originally present. As it would, however, hardly be possible in this case to reduce the hydrolysis completely to zero, the equivalent conductance of the unhydrolyzed salt can not be directly measured, and must therefore be regarded as an unknown quantity, but this can be eliminated by making conductivity measurements with different quantities of acid or base added.

The calculation of the ionization-constant (K_W) of water from the hydrolysis (h) of the salt, which is made approximately by the mass-action expression $K_W = K_A K_B \frac{h^2}{(1-h)^2}$, involves a knowledge of the ionization-constants (K_A and K_B) of the acid and the base. That of acetic acid at the temperatures in question has already been determined by Noyes and Cooper (section 56, Part V); but no data in regard to ammonium hydroxide exist. We therefore first investigated the conductivity of this base at 100° and 156° (making also a few measurements at 51°, 75°, and 125° to assist in applying the temperature corrections); and, in addition, in order to obtain the data for calculating with the help of the law of the independent migration of the ions the equivalent conductance Λ_0 of the completely ionized base, we determined the conductivity of sodium hydroxide and of ammonium chloride at 100° and 156° at low concentrations (0.002 and 0.012 normal). The measurements with sodium hydroxide were extended to 218°, as the data at this temperature were needed in interpreting the results of Noyes and Cooper; and also to the higher concentration of 0.05 normal on account of the interest attaching to the results themselves.

After describing the apparatus and method used in all the experiments and the preparation of the solutions, we will first present the results obtained with the three substances last referred to, and then in separate sections will present and discuss the hydrolysis experiments with ammonium acetate.

61. APPARATUS AND METHOD OF PROCEDURE.

The same bomb was employed as in the investigation of Noyes and Cooper (section 47, Part V) in the form designated by them as cell III, that is, with a cylindrical platinized platinum-iridium electrode. The same heaters were also used. The measurements at 51°, 75°, and 125° with the ammonium hydroxide solutions were made in the liquid xylene bath commonly used at 18°. It was heated electrically by means of a nickel-steel resistance coil immersed in the xylene. The same three thermometers were used in the 18°, 100°, 156°, and 218° baths as before. That used at 156° and 218° was also employed in the few measurements at 125°. The 100° point of the French thermometer (No. 65650) used in the brombenzene and naphthalene vapor-baths was frequently tested by heating in steam in the usual Regnault apparatus. The Beckmann thermometer used in the 100° bath was similarly tested. As in all the preceding researches, the temperatures above 100° were reduced to the hydrogen-gas scale by means of Crafts's table of corrections after modifying them in accordance with the lower value for the boiling point of pure naphthalene found by Jaquerod and Wassmer. A fourth thermometer was employed in determining the temperature of the liquid xylene bath when used at 51° and 75°. This thermometer was standardized by comparison with a thermometer certified by the deutsche physikalisch-technische Reichsanstalt. A new conductivity measuring apparatus of the roller type described by Kohlrausch and Holborn* was employed. It was calibrated as described in the preceding parts. The maximum correction on the bridge-ratio at any point was 0.06 per cent, that on the resistance coils 0.02 per cent, but these corrections were always applied. The induction-coil was a small one of the ordinary form. The procedure followed in the experiments was nearly the same as in the preceding investigation. In filling the bomb with the solutions especial care was taken to avoid contamination from the carbon dioxide of the air. Some of the solution was forced by purified compressed air out of the bottle containing it into a pipette filled with purified air, and this solution was run into the bomb which was kept covered with a perforated watch-glass. (Some of the same solution had usually been left standing in the bomb over night.) The liquid was shaken around the sides of the bomb and poured out by slightly raising the watch-glass. This rinsing process was twice again repeated. Then a quantity of solution sufficient to nearly fill the bomb at the highest temperature (156° or 218°) to which the experiment was to be carried was forced into the pipette (one of suitable capacity, 113 or 104 c.cm., with an appropriate mark on the stem being used), and was run into the bomb, whereupon the watch-glass was removed and immediately replaced by the cover, which had been previously rinsed with solution and placed bottom downwards on washed filtered paper, which removed most of the adhering solution. Experience showed that portions of the same 1/30 normal (or even 1/100 normal) ammonium hydroxide solution, although extremely sensitive to contamination by carbon dioxide, could be successively introduced into the bomb in this way without showing a greater difference in conductance than 0.1 per cent. In the sodium hydroxide experiments, the air pressure in the bomb was reduced after closing it to 2 to 4 cm. mercury, but with the solutions of the other substances (which were carried only to 156°) the air was not exhausted. At each temperature after the bomb had nearly attained the temperature of the bath it was removed, shaken, and at once returned to the bath. After the conductance seemed constant, a series of three readings was made at 5-minute intervals and the mean of these was taken; except that in the case of sodium hydroxide at 218°, where a slow progressive decrease of conductance was observed, the maximum value was taken.[*] In the case of this substance at 218°, moreover, in order to reduce the contamination, the solution was transferred from the 18° directly to the 218° bath, and the values at 100° and 156° were determined by separate experiments. In almost all experiments the conductance was remeasured at 18° after the heatings as a check upon the contamination.

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*Leitvermögen der Elektrolyte, 1898, p. 42, fig. 37.

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[*] That the progressive change was not very large with even a 4-milli-normal sodium hydroxide solution at 218° is shown by the following conductance values obtained with such a solution at the times after the bomb was introduced into the 218° bath that are shown in the first column of the table. Shaking the bomb caused very little change in the conductance.

Time in minutes.	Conductance × 10^6.		
	First experiment.	Second experiment.	Third experiment.
15	22,520	22,780	22,570
19	22,570	22,880	22,620
22	22,520	22,880	22,570
29	22,420	22,470	22,520
39	......	......	22,420

62. PREPARATION OF THE SUBSTANCES AND SOLUTIONS.

Two separate solutions of sodium hydroxide were used in this work. Each was prepared by mixing a solution of sodium sulphate with one of barium hydroxide. These two substances were first purified by crystallizing commercial "chemically pure" samples four times from water. The sodium sulphate was then tested for impurities with negative results by adding ammonia, ammonium carbonate, and sodium phosphate. The barium hydroxide was first tested for silica or other insoluble matter and for other metals than barium, but these were not present in appreciable quantity.* In preparing the sodium hydroxide solutions, a nearly saturated barium hydroxide solution was first made up with conductivity water and filtered into a tared 7-liter bottle filled with carbon-dioxide-free air; the exact strength of this solution was next determined by titrating a portion with standard hydrochloric acid, and the quantity of it was ascertained by weighing the bottle; a quantity of sodium sulphate equivalent to the barium hydroxide was then weighed out, dissolved in water, and run into the bottle. After the precipitate had settled, two portions of the clear solution were drawn out, and one was analyzed for barium by neutralizing with sulphuric acid and adding considerable sodium sulphate, the other for sulphate by neutralizing with hydrochloric acid and adding considerable barium chloride.† Then a quantity of sodium sulphate or of barium hydroxide solution corresponding to the excess of barium or sulphate thus found to be present was added to the main solution; and this solution, after the precipitate had completely settled, was forced over into a clean dry bottle. Throughout these operations and in the subsequent use of the solution any air that was admitted to the bottle had to bubble through potash solution and soda-lime tubes. The final solution contained less than 0.1 per cent of barium sulphate (expressed in equivalents and referred to the sodium hydroxide present).‡ It was standardized by weight using phenolphthalein as an indicator against a pure hydrochloric acid solution whose content had been determined by precipitation with silver nitrate to be 137.37 milli-equivalents per kilogram of solution.*

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*This was done by evaporating 5 grams of the solution with hydrochloric acid, dissolving the salt in water, and collecting the residue, which was found to weigh 2.5 mg. or 0.05 per cent of the original weight, but of this only 0.5 mg. or 0.01 per cent volatilized with hydrofluoric acid. To the filtrate from the residue a slight excess of sulphuric acid was added, the precipitate filtered out, the filtrate evaporated, and the residue ignited and weighed; it was found to weigh only 1 mg. or 0.02 per cent.

†Thus in the case of the second solution so prepared, there was found to be an excess of barium of 0.13 and of sulphate of 0.08 milli-equivalents per kilogram; and therefore 0.05 milli-equivalents of sodium sulphate were added for each kilogram of solution.

‡Thus it follows from the data of the preceding note that the second solution contained 0.08 milli-equivalents $BaSO_4$ per kilogram, which is 0.08 per cent of the NaOH present (105.3 milli-equivalents).

Solution No. 1 was thus found to contain 151.00 milli-equivalents NaOH per kilogram; solution No. 2, 105.32 milli-equivalents. The more dilute solutions (0.05 to 0.002 normal), whose conductance was actually measured, were prepared from these stock solutions by adding weighed portions of them to weighed quantities of water. The water used for 50 and 20 milli-normal solutions had a specific conductance at 18° of 0.9×10^{-6}; that used for the diluter solutions one of 0.6×10^{-6}. Two or three independently diluted solutions were always prepared at the concentrations of 4- and 2-milli-normal. The reduction of content from milli-equivalents per kilogram to milli-equivalents per liter at 4° was made with the help of the specific gravity (1.002) in the case of the 50 milli-normal solution; but this correction was insignificant and was not applied in the case of the more dilute solutions.†

Three separate stock solutions of ammonium hydroxide, each approximately 0.1 normal, were prepared in the course of the work from water of conductivity $0.5 - 0.8 \times 10^{-6}$ and from a "strictly chemically pure" sample of ammonia water (sp. gr. 0.90) furnished by Baker and Adamson of Easton, Pennsylvania, and stated to be free from amines and hydrocarbons. Ten cubic centimeters of the strong ammonia yielded only 1 mgm.

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*Derived from the following data:

Grams solution taken	112.34	106.58	91.31
Grams AgCl obtained	2.2121	2.0988	1.7994
Milli-equiv. per kilogram	137.34	137.34	137.44

The weights of silver chloride were reduced to vacuo. The atomic weights used were Ag = 107.93, Cl = 35.45. The equivalent conductance of the solution was also determined at 18° in a U-shaped cell and found to be 348.0 while Goodwin and Haskell (Phys. Rev., **19**, 382, 1904) found 347.8 for the same solution.

†After the conductance measurements were completed 481.3 grams of the second solution were (December 12, 1904) acidified with hydrochloric acid, evaporated to dryness, and the residue was heated to 200° and weighed; it amounted to 2.997 grams, which if regarded as NaCl would correspond to a content of 106.5 millimols per kilogram solution while that found earlier by titration was 105.3. Exactly one-half of this excess of 1.1 per cent was found to be due to silica (or some other substance insoluble in strong acid), which had apparently been taken up from the bottle since the solution was first prepared (October 22, 1904). About one-half of the remainder consisted of barium sulphate or sodium sulphate; for this amount was precipitated when barium chloride was added to the filtrate from the silica after evaporation to remove the acid present. These impurities certainly could not have nearly so great a percentage effect on the conductance as upon the total solid-content, both because of their having a lesser equivalent conductance than the base, and because they tend to compensate each other, acids like silica reducing and salts increasing the conductance. Still their presence might possibly give rise to an error of 0.5 per cent in the equivalent conductance of the base. That the stock solution was not much contaminated with carbonic acid was shown by the fact that even at the end of the measurements it gave no precipitate with a large quantity of barium hydroxide. The conductance of a 2-millimolal solution prepared from the second stock solution on December 1 to 4 was greater than that of one so prepared on November 10 by only 0.2 per cent at 18°, which is within the experimental error at that concentration, showing that little if any change with the time took place.

of residue; and a combustion of 0.86 grams of solution (containing 0.50 gram or 14.3 millimols NH_4OH) gave 2.2 mg. $BaCO_3$* corresponding to 0.5 mg. or 0.011 millimol CO_2. Special precautions were taken to exclude carbon dioxide in diluting the solution. Neither the original sample nor the stock solution prepared from it gave the slightest turbidity with barium hydroxide even on standing. The absence of any considerable impurity is also confirmed by the agreement (within 0.01 per cent) of the conductance of the stock solutions with that of one prepared by R. B. Sosman in this laboratory from liquid ammonia distilled from sodium. The three separate solutions prepared by us at different times also agreed in conductance within 0.1 per cent. These stock solutions were standardized by titration, using methyl orange as an indicator, against a new hydrochloric acid solution which by precipitation with silver nitrate was found to contain 115.38 milli-equivalents per kilogram solution.† The more dilute solutions (30 and 10 milli-normal) were prepared from weighed portions of the stock solutions by adding weighed quantities of water of specific conductance 0.5×10^{-6} entirely out of contact with air containing carbon-dioxide. No correction was applied to reduce the content-by-weight to volume concentration at 4°, since this amounted to less than 0.1 per cent even with the 100 milli-normal solution. The concentrations of the three stock solutions in milli-equivalents per liter at 4° were as follows: No. 1, 97.07; No. 2, 99.90; No. 3, 102.59.‡

The ammonium chloride used was made by neutralizing some of the "strictly chemically pure" ammonia water above referred to with freshly distilled "chemically pure" hydrochloric acid, and crystallizing the salt three times from hot water by cooling. The salt was dried by heating in an open

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*The products of combustion were passed through barium hydroxide solution and the precipitate filtered off out of contact with the atmosphere and weighed.

†Derived from the following data:

Solution taken (grams).	103.55	104.31	148.07	103.17	104.6
AgCl obtained (grams).	1.7139	1.7272	2.451	1.7094	1.722
Millimols per kilogram.	115.44	115.48	115.46	115.56	115.5

The mean of these values is 115.49, which reduced to vacuo becomes 115.38. The equivalent conductance at 18° was found to be 349.9 while the value of Goodwin and Haskell interpolated for this concentration is 350.2.

‡Derived from the following data:

Stock Solution No. 1:

Solution taken (grams).	182.78	178.86	119.07
HCl solution used do. .	153.79	150.51	100.16
Milli-equiv. per kilogram.	97.07	97.08	97.06

The mean of these values is 97.07.

Stock Solution No. 2:

Solution taken (grams).	162.25	133.78	116.65
HCl solution used do. .	140.51	115.84	100.95
Milli-equiv. per kilogram.	99.92	99.91	99.87

The mean of these values is 99.90.

Stock Solution No. 3:

Solution taken (grams).	161.77	179.50	116.47
HCl solution used do. .	143.84	159.63	103.53
Milli-equiv. per kilogram.	102.59	102.61	102.58

The mean of these values is 102.59.

dish in a slow current of dry air at 105°. The loss of weight became continuous and quite uniform being due doubtless to vaporization of the salt. A nearly 0.1 normal solution was made by weighing out the salt and dissolving in a weighed quantity of water. The exact content was 93.56 millimols per kilogram solution, and this agreed closely with the content (93.64) determined as a check by precipitation with silver nitrate.* In most of the experiments with this salt about $\frac{1}{10}$ an equivalent of ammonium hydroxide for each equivalent of salt was added, in order to make the hydrolysis inappreciable. The ammonium hydroxide solution used for this purpose was a fourth one, about 0.1 normal, freshly prepared from the strong ammonia; its conductance was about the same as that of the other solutions when freshly prepared.

A stock solution of ammonium acetate, approximately 50 milli-normal, was prepared by mixing a definite weight of ammonium hydroxide solution (No. 3), with that weight of an approximately 100 milli-normal acetic acid solution which contained a quantity of the acid exactly equivalent to the base. This acetic acid solution was made by diluting with water of specific conductance 0.8×10^{-6} glacial acetic acid purified by fractional freezing and by distillation. It was standardized, using phenolphthalein as an indicator against a barium hydroxide solution which had been titrated against the hydrochloric acid solution last referred to. The exact concentration of this acetic acid solution was 105.58 milli-equivalents per liter at 4° (105.44 at 18°) and its equivalent conductance (not corrected for the conductance of the water) was 4.57. The value obtained by Noyes and Cooper (interpolated by the equation $\Lambda^2 C = \text{const.}$) for this concentration was 4.55, in as good agreement as could be expected with entirely independent samples and solutions.

63. THE CONDUCTANCE-CAPACITY OF THE APPARATUS.

The conductance-capacity of the bomb was determined by measuring the actual conductance at 17.93° of 0.02 and 0.01 normal potassium chloride solutions prepared by dissolving 1.4910 or 0.7455 gm. of salt (weighed in air) in one liter of water (of conductivity $0.7 - 0.9 \times 10^{-6}$ at 18°) at 18°, and dividing this after correcting for temperature and conductance of the water into the specific conductances of these solutions (2399 or 1224.3×10^{-6}) corresponding to the equivalent conductances at 18° given by Kohlrausch and Maltby† (119.96 or 122.43).

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*As shown by the following data:

Solution taken (grams).	89.51	98.64	122.61
AgCl obtained (grams).	1.2030	1.3250	1.6481
Millimols per kilogram.	93.74	93.69	93.75

The mean is 93.73 or when the weights are reduced to vacuo it becomes 93.64.

†Landolt-Börnstein-Meyerhoffer, Tabellen, 744 (1905).

The following are the data of these determinations, all of which were made at 17.93°:

Table 47.—*Conductance-capacity of the bomb.*

Date.	Milli-equivalents per liter at 18°.	Conductance × 10^6.		Conductance-capacity.
		Observed.	Corrected.*	
Sept. 30, 1904......	20.00	16,176	16,194	0.14812
Sept. 30, 1904......	"	16,183	16,201	
Feb. 16, 1905......	"	16,190	16,209	0.14802
Feb. 16, 1905......	"	16,188	16,207	
Feb. 16, 1905......	10.00	8,269	8,276	0.14791
Feb. 16, 1905......	"	8,271	8,278	
June 4, 1905......	10.00	8,268	8,274	0.14795
June 4, 1905......	"	8,269	8,275	
Final mean......	......	......	......	0.14800

* To 18° and for the conductance of the water.

It is evident from these results that the change of the conductance-capacity with the time and the difference in the values of it determined with the two solutions is trivial. The mean value, 0.14800, is therefore employed in all the calculations of this article.

The change of the conductance-capacity with the temperature was calculated by the method and with the help of the data described in section 36, Part IV. The only really significant factor in this case determining the correction was the expansion of the platinum-iridium electrode, which had a height of 9.81 mm. and a diameter of 7.19 mm. The computation shows that the conductance-capacity at 18° should be decreased by the following percentage amounts at the following temperatures: 50° by 0.05; 75° by 0.07; 100° by 0.10; 125° by 0.14; 156° by 0.18; and at 218° by 0.26. These corrections were always applied.

Measurements of some of the sodium hydroxide solutions were also made in a U-shaped vessel. The conductance-capacity of this was determined by measuring in it a 0.1 normal solution of potassium chloride made by dissolving 7.455 grams of the salt (weighed in air) in one liter of water at 18°. The equivalent conductance of this solution was taken to be 112.03 as given by Kohlrausch and Maltby. As an accident happened to one of the electrodes in the course of the experiments, the capacity had to be redetermined, so that there are two values designated "Cell I" and "Cell II." The data obtained at 17.93° are given in table 48.

TABLE 48.—*Conductance-capacity of the U-shaped vessel.*

Date.	Cell.	Conductance × 10^6.		Conductance-capacity.
		Observed.	Corrected to 18°.	
1904				
Oct. 17....	I	1,322.9	1,324.9	8.456
Oct. 17....	I	1,322.8	1,324.8	
Nov. 4....	II	1,318.4	1,320.4	8.489
Nov. 4....	II	1,317.6	1,319.6	

64. THE WATER CORRECTION.

Since impurities in the water tend to decrease the conductance of strong bases, no correction for the conductance of the water was applied to the results with sodium hydroxide. Nor was any correction applied to those with the 1/40 normal ammonium acetate solution, since the correction was less than 0.05 per cent. In the other cases (the ammonium hydroxide and chloride and 1/100 normal ammonium acetate solutions) a correction was applied, which was determined by heating pure water in the bomb (after it had been freed as far as possible from absorbed substance by a previous heating at 156° with water), making the time of heating at each temperature the same as in the usual experiments. The results obtained are shown in table 49.

TABLE 49.—*Actual conductance* (×10^6) *of water in the bomb.*

Date.	18°		100°		156°.
	Initial.	Final.	Initial.	Final.	
1905					
June 5...	3.1	4.8	13.0	15.3	23.9
June 6...	5.7	5.9	15.7	....	27.2
June 7...	3.4	4.7	13.7	....	24.9
Mean ...	4.1	5.2	14.1	15.3	25.3

These corrections were subtracted from the observed conductance of the solutions in the cases specified above. They form roughly the following fraction of that conductance in the different cases:

Substance.	Milli-equivalents per liter.	Temperature.	Percentage correction.
NH_4OH	100	18	—0.2
"		156	—0.5
"	10	18	—0.6
"		156	—1.8
NH_4Cl	2	18	—0.2
"		156	—0.3
$NH_4C_2H_3O_2$	100	156	—0.1

65. CONDUCTIVITY DATA FOR THE SOLUTIONS OF SODIUM HYDROXIDE, AMMONIUM HYDROXIDE, AND AMMONIUM CHLORIDE.

The following tables contain the direct results of the observations and the equivalent conductances computed therefrom. These original data are presented as a matter of record. All of interest that they contain will be seen in a more obvious way from the summary presented and discussed in the next section.

The measurements with 20 and 50 milli-normal sodium hydroxide solutions are affected by an error arising from the polarization due to the small resistance of these solutions in the bomb. An accurate correction for this error can not be made, but to estimate its magnitude approximately three fairly strong solutions of the base (21, 50, and 75 milli-normal) were measured at 18° both in the bomb and in the U-shaped vessel above referred to and designated cell I or cell II, in which the conductance was only about one-sixtieth as great. The results of these measurements are first presented in table 50.*

TABLE 50.—*Conductivity data for sodium hydroxide in different vessels.*

Date.	Stock Sol. No.	Cell.	Concentration at 18°.	Conductance $\times 10^6$.	Equivalent conductance.	
					Separate values.	Mean.
Oct. 19...	1	Bomb...	76.5	101,490 101,430	196.24 196.12	196.18
Oct. 19... Oct. 20...	1	Cell I...	76.5	1,783.4 1,785.0	197.08 197.26	197.17
Nov. 11..	2	Bomb...	50.22	67,850 67,800	199.9 199.8	199.85
Nov. 11.. Nov. 12..	2	Cell II...	50.22	1,187.0 1,186.8	200.7 200.6	200.65
Nov. 9...	2	Bomb...	21.06	29,250 29,230 29,240	205.6 205.4 205.5	205.50
Nov. 7...	2	Bomb...	21.50	29,880 29,840	205.7 205.4	205.55
Nov. 8...	2	Cell II..	21.50	520.3 520.8	205.5 205.6	205.55

It is evident from these results that when the conductance in the bomb does not exceed $30{,}000 \times 10^{-6}$ the difference between the equivalent conductance derived from it and that derived from the measurement in the U-shaped cell is inconsiderable; but that the difference is 0.5 per cent when the conductance is $100{,}000 \times 10^{-6}$. Although it is uncertain whether this difference between the true value and that derived from the measurement in the bomb would be substantially the same at different temperatures, and whether it would be proportional to the conductance of the solution, it has nevertheless seemed to us that values nearer the truth would be obtained by applying a correction to our results with sodium hydroxide in accordance with these assumptions than by leaving them uncorrected; for there is certainly some error in this direction. We recognize, however, that there may still be an error in the corrected results as great as the correction applied; and it is expected that more accurate data will be later obtained with a bomb containing the electrode within a cup to increase the resistance. The percentage correction actually applied was equal to 5 times the conductance measured in the bomb; that is, it was 0.5 per cent when the conductance was $100{,}000 \times 10^{-6}$, 1 per cent when it was $200{,}000 \times 10^{-6}$, etc. This correction has been introduced in table 51 in the process of calculating the equivalent conductance from the observed conductance.

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*Those on October 19-20, 1904, were made with a solution prepared by diluting stock solution No. 1, which was then three months old. The absolute values are therefore not accurate.

The results obtained in the bomb with the solutions of sodium hydroxide, ammonium hydroxide, and ammonium chloride are given in tables 51-53.

The first column gives the date of the experiment; the second, the concentration at 4° in milli-equivalents per liter (the number of milli-equivalents being based upon the atomic weights referred to oxygen as 16.000 and weights being reduced to vacuo); the third, the temperature corrected for thermometric error at which the conductance was measured; the fourth, the concentration at the temperature of the measurements, calculated by dividing the concentration at 4° by the corresponding specific-volume ratio[*] and in the case of the sodium hydroxide measurements at 156° applying the correction for the solvent in the vapor space;[†]

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[*] The specific-volume ratio (that is, the ratio of the specific volume of the solution at the temperature of the measurements to that at 4°) was assumed to be identical with that of pure water, the values determined by Noyes and Coolidge being used at 218°. This assumption is justified since they showed that up to 218° the expansion of a 0.1 normal sodium chloride solution is identical with that of a 0.002 normal solution. The values of the ratio are 1.0013 at 18°, 1.0125 at 51°, 1.0257 at 75°, 1.0432 at 100°, 1.0660 at 125°, 1.0978 at 156°, and 1.1862 at 218°.

[†] Since the bomb was usually filled so as to have a vapor-space of only 1 or 2 c.cm. at either 156° or at 218°, the correction for the amount of the liquid vaporized was insignificant and was not as a rule applied, the only exception being in the case of the sodium hydroxide solutions at 156° where the vapor space was about 11 c.cm. and where the concentration was correspondingly increased by 0.04 per cent. In the case of the ammonia solutions the possibility existed that the solute also passed into the vapor space in appreciable quantity; but this was disproved by comparative conductivity measurements made with varying quantities (76 and 113 c.cm. at 18°) of solution in the bomb. Thus, a 97.07 millimolal NH_4OH solution showed in the bomb the following conductances, the usual procedure in heating being followed in each case: 4969 and 4972, mean **4970** at 100°; 4735 and 4735, mean **4735** at 156°, when 113 c.cm. at 18° were introduced: and 4964 and 4977, mean **4970**, at 100°; and 4675 and 4703, mean **4689** at 156°, when 76 c.cm. at 18° were introduced. There is seen to be no difference at 100° and one of only 1 per cent at 156°. Since the latter arises from a difference in vapor-space of 40 c.cm., it is evident that the error would be inappreciable when the vapor-space was, as was usual, about 1 c.cm.

the fifth, the measured conductance in reciprocal ohms, multiplied by 10^6 and corrected for the instrumental errors — those in the slide wire and the resistance coils and for the lead resistance (0.03 ohm); the sixth, the equivalent conductance calculated from the value of the conductance in the fifth column by applying the water correction (in the cases specified in the last section), multiplying by the conductance-capacity,* and dividing by the concentration given in the fourth column (also in the case of the 0.019 and 0.049 normal sodium hydroxide solutions applying the correction for polarization described in the text following the experiments with this substance). In the experiments with ammonium chloride, a small quantity (about one-tenth as many equivalents) of ammonium hydroxide were added in order to eliminate entirely the hydrolysis possible in such dilute solutions at the higher temperatures; the tables therefore contain additional columns giving the concentration of this substance and the conductance of the solution corrected for that of the ammonium hydroxide, which correction was calculated by the mass-action expression $\frac{C_B}{C_S} K_B \Lambda_0$ in which C_B and C_S represent the concentration of the base and salt respectively, K_B the ionization-constant of the base (section 69, table 64), and Λ_0 its equivalent conductance when completely ionized (section 67, table 59).

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*Unless otherwise stated, all measurements were made in the bomb, whose conductance-capacity (constant throughout the whole series of experiments) was given for each temperature in section 63.

Table 51.—*Conductivity data for sodium hydroxide.*

FROM STOCK SOLUTION No. 1 (PREPARED JULY 20, '04.)

Date.	Concentration at 4°.	Temperature ($t°$)	Concentration at $t°$.	Conductance × 10^6.	Equivalent conductance.
1904					
Aug. 17....	19.151	17.93	19.127	26,780	207.4
		217.2	16.158	102,340	940.0
		17.93	19.127	26,630	206.2
Aug. 18....	19.151	17.93	19.127	26,900	208.3
		217.4	16.154	102,430	941.0
		17.93	19.127	26,650	206.4
Aug. 18....	19.151	17.93	19.127	26,820	207.7
		217.4	16.154	102,490	941.6
		17.93	19.127	26,550	205.6
Aug. 19....	19.151	17.93	19.127	26,800	207.6
		100.12	18.357	69,760	562.4
		156.1	17.449	91,060	774.5
		100.08	18.157	69,600	562.7
		17.93	19.127	26,790	207.5
Aug. 20....	19.151	17.93	19.127	26,790	207.5
		100.20	18.356	69,410	561.19
		155.6	17.864	90,880	772.7
		100.20	18.356	69,360	560.80
		17.93	19.127	26,743	207.1
Aug. 22....	19.151	100.20	18.356	69,290	560.23
		155.6	17.457	90,880	772.7
		217.5	16.151	102,200	939.1
		155.6	17.457	90,160	766.6
		100.20	18.356	98,260	551.91
Aug. 24....	49.08	17.93	49.02	66,670	201.9
		100.18	47.89	171,640	543.84
		155.7	44.74	223,500	746.0
Aug. 25....	49.08	17.93	49.02	66,630	201.7
		100.16	47.89	171,240	542.5
		155.6	44.74	220,100	734.6
		217.4	41.38	245,600	886.5
		155.6	44.74	221,200	738.7
		100.16	47.89	169,720	537.8
		17.93	49.02	65,890	199.5
Aug. 26....	49.08	17.93	49.02	66,770	202.1
		100.16	47.89	171,500	543.3
		155.6	44.74	223,600	746.1
		100.16	47.89	171,520	543.5
		17.93	49.02	66,710	202.00
Aug. 30....	49.08	17.93	49.02	66,530	201.4
		217.7	41.38	247,200	892.8
		17.93	49.02	66,140	200.2
Aug. 30....	49.08	17.93	49.02	66,510	201.4
		217.7	41.38	247,200	892.8
		17.93	49.02	66,290	200.7
Aug. 31....	49.08	17.93	49.02	66,604	201.6
		155.6	44.74	221,800	740.3
		17.93	49.02	66,530	201.4

TABLE 51.—*Conductivity data for sodium hydroxide*—Continued.

FROM STOCK SOLUTION No. 2 (PREPARED OCT. 22, ANALYZED NOV. 3).

Date.	Concentration at 4°.	Temperature ($t°$)	Concentration at $t°$.	Conductance × 10^6.	Equivalent conductance.
1904					
Nov. 17....	3.974	17.93	3.970	5,669	211.4
		218.3	3.344	2,266	999.1
Nov. 18....	3.974	17.93	3.970	566.3	211.1
		218.2	3.344	2,262	997.4
		17.93	3.970	534.6	199.28
Nov. 19....	3.974	17.93	3.970	566.7	211.3
		100.05	3.810	1,490.8	578.4
		155.6	3.622	1,967.4	802.3
		17.93	3.970	563.6	210.1
Nov. 22....	4.401	17.93	4.395	629.8	212.1
		217.5	3.707	2,501.	994.4
		17.93	4.395	613.2	206.5
Nov. 23....	4.026	17.93	4.021	573.5	211.1
		217.3	3.392	2,291.	995.6
		17.93	4.021	562.4	207.0
Nov. 25....	4.026	17.93	4.021	573.8	211.2
		99.57	3.861	1,501.1	574.7
		155.5	3.669	1,989.7	801.0
		99.61	3.861	1,498.3	573.6
		17.93	4.021	572.3	210.6
Nov. 26....	4.026	17.93	4.021	574.3	211.4
		99.90	3.860	1,507.2	577.2
		155.8	3.668	1,995.2	803.4
		99.90	3.860	1,504.2	576.1
		17.93	4.021	573.5	211.1
Nov. 29....	3.972	17.93	3.967	566.8	211.5
		217.7	3.346	2,259.	995.2
		17.93	3.967	550.6	205.4
Nov. 30....	3.972	17.93	3.967	564.2	210.5
		99.71	3.809	1,478.6	573.9
		156.1	3.617	1,966.5	803.0
		99.68	3.809	1,475.9	572.8
		17.93	3.967	562.4	209.8
Dec. 1......	2.069	17.93	2.066	296.3	212.2
		99.79	1.9839	779.8	581.1
		155.6	1.8853	1,035.5	811.3
		99.81	1.9839	778.5	580.1
		17.93	2.066	294.6	211.0
Dec. 2......	2.069	17.93	2.066	295.5	211.6
		100.15	1.9832	780.5	581.8
		155.9	1.8848	1,035.2	811.3
		100.12	1.9832	778.1	580.0
		17.93	2.066	293.5	210.2
Dec. 3......	1.9925	17.93	1.9900	285.1	212.0
		100.25	1.9098	753.4	583.1
		156.2	1.8147	1,000.0	814.0
		100.22	1.9098	750.6	581.0
		17.93	1.9900	283.6	210.9
Dec. 4......	1.9925	17.93	1.9900	284.3	211.4
		100.04	1.9102	752.3	582.2
		155.9	1.8152	999.5	813.3
		100.02	1.9102	749.6	580.1
		17.93	1.9900	282.5	210.1

TABLE 52.—*Conductivity data for ammonium hydroxide.*

FROM STOCK SOLUTION No. 1 (PREPARED JANUARY 9, 1905.)

Date.	Concentration at 4°.	Temperature, t°.	Concentration at t°.	Conductance $\times 10^6$.	Equivalent conductance.
1905					
Jan. 13†...	32.44	17.93	32.40	1,190.9	5.422
		99.88	31.10	2,811	13.297
		156.2	29.54	2,625	13.005
Jan. 14....	32.44*	17.93	32.40	1,189.5	5.415
Jan. 16....	32.44	17.93	32.40	1,193.5	5.433
		155.6	29.56	2,651	13.130
Jan. 17....	33.08	17.93	33.04	1,204.4	5.377
		99.77	31.71	2,841	13.175
		156.0	30.13	2,670	12.978
		17.93	33.04	1,175.4	5.241
Jan. 18....	33.08	17.93	33.04	1,205.2	5.381
		100.03	31.71	2,851	13.224
		156.6	30.11	2,673	12.990
		17.93	33.04	1,196.7	5.337
Jan. 20....	33.07	17.93	33.03	1,203.8	5.375
		99.74	31.71	2,847	13.203
		155.6	30.14	2,670	12.966
Jan. 21....	33.07	17.93	33.03	1,211.6	5.410
		99.98	31.70	2,863	13.282
		155.9	30.13	2,699	13.104
Jan. 27....	33.05	17.93	33.01	1,207.3	5.394
		99.91	31.69	2,860	13.277
Jan. 28....	33.05	17.93	33.01	1,207.1	5.394
		99.80	31.69	2,870	13.320
		157.1	30.06	2,705	13.160
		99.76	31.69	2,864	13.284
		17.93	33.01	1,205.3	5.380
Jan. 30....	33.05	17.93	33.01	1,207.3	5.394
		100.20	31.68	2,869	13.320
		156.2	30.09	2,710	13.173
		100.28	31.68	2,871	13.326
		17.93	33.01	1,204.8	5.378
Jan. 31....	97.07	17.93	96.95	2,078	3.166
		100.23	93.04	4,954	7.850
		156.3	88.37	4,657	7.742
		100.18	93.05	4,950	7.841
		17.93	96.95	2,075	3.161
Feb. 1....	97.07	17.93	96.95	2,078	3.166
		99.95	93.07	4,968	7.870
		155.8	88.41	4,733	7.865
		99.91	93.07	4,981	7.889
		17.93	96.95	2,082	3.172
Feb. 3....	97.07	17.93	96.95	2,082	3.172
		99.93	93.07	4,971	7.874
		155.9	88.40	4,733	7.867
		99.95	93.07	4,981	7.889
		17.93	96.95	2,083	3.173
Feb. 9....	9.9085	17.93	9.896	655.5	9.740
		99.91	9.500	1,558.1	24.02
		156.4	9.019	1,480.8	23.84
		99.85	9.500	1,539.2	23.71
		17.93	9.896	647.2	9.603

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*Where the concentration was the same in successive measurements they were made with different portions of the same diluted solution.

†In the experiments of January 13-21, only 103 c.cm. solution were put into bomb, while in all later experiments 113 c.cm. were introduced. The air was not in any case exhausted.

TABLE 52.—*Conductivity data for ammonium hydroxide*—Continued.

Date.	Concentration at 4°.	Temperature, t°.	Concentration at t°.	Conductance $\times 10^6$.	Equivalent conductance.
FROM STOCK SOLUTION No. 1 (PREPARED JANUARY 9, 1905.)					
Feb. 10...	9.9085	17.93	9.896	655.2	9.735
		99.52	9.504	1,560.3	24.03
		156.5	9.019	1,480.2	23.83
		99.54	9.504	1,544.7	23.78
		17.93	9.896	647.3	9.605
STOCK SOLUTION No. 1 (WHEN 35 DAYS OLD).					
*Feb. 11..	97.07	17.93	96.95	2,096	3.193
		100.10	93.06	5,032	7.975
*Feb. 13..	97.07	17.93	96.95	2,097	3.194
		99.07	93.14	5,044	7.985
		155.4	88.44	4,840	8.043
		99.13	93.15	5,041	7.981
		17.93	96.95	2,101	3.200
Feb. 14...	97.07	17.93	96.95	2,095	3.192
		99.86	93.07	5,042	7.988
		156.4	88.36	4,822	8.021
		99.81	93.08	5,046	7.994
		17.93	96.95	2,097	3.193
FROM STOCK SOLUTION No. 2 (PREPARED FEBRUARY 20, 1905.)					
Feb. 21...	99.90	17.93	99.77	2,095	3.101
		100.07	95.77	4,956	7.629
		156.6	90.92	4,629	7.479
		17.93	99.77	2,096	3.100
Feb. 23...	99.90	17.93	99.77	2,094	3.100
		99.92	95.79	4,965	7.641
		156.4	90.93	4,663	7.532
		99.85	95.79	4,981	7.663
		17.93	99.77	2,094	3.098
Feb. 24...	99.90	17.93	99.77	2,094	3.099
		155.6	91.00	4,657	7.516
					(7.549)
		17.93	99.77	2,089	3.092
Feb. 25...	33.29	17.93	33.24	1,211.7	5.375
		99.52	31.93	2,863	13.200
		155.4	30.33	2,706	13.058
		17.93	33.24	1,210.0	5.366
Feb. 27...	9.853	17.93	9.841	651.5	9.735
		99.64	9.451	1,548.4	23.83
		155.7	8.975	1,454.6	23.52
		17.93	9.841	646.8	9.650
Feb. 28...	9.853	17.93	9.841	651.9	9.741
		99.59	9.450	1,543.2	23.92
		155.8	8.974	1,457.0	23.56
		99.64	9.449	1,534.7	23.76
		17.93	9.841	646.5	9.645

*Although every precaution was taken to preserve this stock solution, the results of these experiments of February 13 and 14 when compared with those of January 31 to February 8 show that contamination had suddenly taken place. They are included here merely to illustrate the great effect especially at the higher temperatures of what must have been a minute contamination; this effect consisted in this case of an increase of about 0.8 per cent at 18° and of 2.5 per cent at 156°. That it was not due to contamination in transferring the solution to the bomb is shown by the excellent agreement of the three earlier and of the two later values among themselves.

TABLE 52.—*Conductivity data for ammonium hydroxide*—Continued.

STOCK SOLUTION No. 3 (PREPARED MARCH 16, 1905.)					
Date.	Concentration at 4°.	Temperature, $t°$.	Concentration at $t°$.	Conductance × 10^6.	Equivalent conductance.
Mar. 17...	102.59	17.93	102.46	2,121	3.057
		75.20	100.01	4,540	6.700
		100.02	98.35	5,018	7.521
		124.8	96.24	5,072	7.760
		17.93	102.46	2,120	3.055
Mar. 18...	102.59	17.93	102.46	2,120	3.056
		51.00	101.30	3,709	5.404
		75.20	100.01	4,543	6.704
		99.60	98.39	5,010	7.506
		124.8	96.24	5,069	7.755
		17.93	102.46	2,117	3.050

TABLE 53.—*Conductivity data for ammonium chloride.*

Date.	Concentration at 4°.		Temperature, $t°$.	Concentration at $t°$.		Conductance × 10^6.		Equivalent conductance.
	NH_4Cl.	NH_4OH.		NH_4Cl.	NH_4OH.	Observed.	Corrected for NH_4OH.	
1905								
May 17....	12.492	0.00	17.93	12.474	......	10,233	......	121.31
May 17....	12.492	0.00	17.93	12.474	......	10,233	......	121.31
May 18....	12.513	1.486	17.93	12.497	1.485	10,264	10,261	121.47
			99.52	12.000	1.425	30,690	30,690	377.9
			155.5	11.403	1.354	43,820	43,820	567.4
			17.93	12.497	1.485	10,270	10,267	121.54
May 19....	12.523	1.389	17.93	12.506	1.387	10,273	10,270	121.49
			99.53	12.011	1.332	30,720	30,720	378.0
			155.3*	11.415	1.265	43,880	43,880	567.6
			99.55	12.011	1.332	30,700	30,700	377.7
			17.93	12.506	1.387	10,271	10,267	121.46
May 20....	1.9791	0.2228	17.93	1.9766	0.223	1,691.5	1,688.5	126.43
			99.73	1.8978	0.214	5,108	5,102	397.5
			155.6	1.8036	0.203	7,369	7,365	603.5
			17.93	1.9766	0.223	1,709.0	1,706.0	127.74
May 24....	2.076	0.2383	17.93	2.0730	0.238	1,772.9	1,769.9	126.34
			100.06	1.9900	0.228	5,385	5,379	399.6
			155.9	1.8910	0.217	7,743	7,739	604.8
			100.06	1.9900	0.228	5,417	5,411	402.0
			17.93	2.0730	0.238	1,788.6	1,785.6	127.47

66. SUMMARY AND DISCUSSION OF THE EQUIVALENT-CONDUCTANCE VALUES AND THEIR CORRECTION TO ROUND TEMPERATURES.

The following tables present the equivalent conductance values corresponding to round temperatures calculated from the values given in the previous tables with the help of temperature-coefficients obtained by plotting graphically the conductance values at each concentration at the different temperatures (including those at 51°., 75.2°, and 124.8° in the case of ammonium hydroxide). The values obtained from the measurements at each temperature before going to a higher one are headed "Initial"; and those on coming back, "Final."

TABLE 54.—*Equivalent conductance of sodium hydroxide at round temperatures.*

Date.	Concentration at 4°.	18°		100°		156°		218°.
		Initial.	Final.	Initial.	Final.	Initial.	Final.	
1904								
Aug. 24....	49.08	202.2	......	543.2	......	747.0	......	......
Aug. 25....	49.08	202.0	199.8	542.0	537.2	*736.0	740.1	887.9
Aug. 26....	49.08	202.4	202.2	542.8	542.9	747.4	......	......
Aug. 30....	49.08	201.7	200.5	......	......	......	......	893.5
Aug. 30....	49.08	201.7	201.0	......	......	......	......	893.5
Aug. 31....	49.08	201.9	201.7	......	......	741.6	......	......
Mean ...	49.08	202.09	†200.4	542.7	†542.8	745.3	740.1	891.6
Nov. 11....	50.31	‡200.65	§202.0	......	§537.2	......	......	......
Aug. 17....	19.151	207.7	206.5	......	......	......	......	941.6
Aug. 18....	19.151	208.6	206.7	......	......	......	......	942.2
Aug. 18....	19.151	208.0	205.9	......	......	......	......	942.8
Aug. 19....	19.151	207.9	207.8	561.9	562.4	774.2	......	......
Aug. 20....	19.151	207.8	207.4	560.4	560.0	774.1	......	......
Aug. 22....	19.151	......	......	559.4	551.1	774.0	768.0	940.3
Mean ...	19.151	208.0	†206.4	560.6	†561.3	774.1	768.0	941.7
Nov. 8....	21.55	‡205.55	§207.6	......	§551.1	......	......	......
Nov. 17....	3.974	210.7	......	......	......	......	......	998.3
Nov. 18....	3.974	211.4	*199.6	......	......	......	......	996.9
Nov. 19....	3.974	211.6	210.4	578.2	......	803.7	......	......
Nov. 22....	4.401	212.4	206.8	......	......	......	......	995.7
Nov. 23....	4.026	211.4	207.3	......	......	......	......	997.5
Nov. 25....	4.026	211.5	210.9	576.6	575.3	802.8	......	......
Nov. 26....	4.026	211.7	211.4	577.6	576.5	804.1	......	......
Nov. 29....	3.972	211.8	205.7	......	......	......	......	996.0
Nov. 30....	3.972	210.8	210.1	575.2	574.2	802.7	......	......
Mean ...	4.038	211.5	§210.9 †206.7	576.9	575.3	803.3	......	996.9
Dec. 1.....	2.069	212.5	211.3	582.0	580.9	812.5	......	......
Dec. 2.....	2.069	211.9	210.5	582.4	580.5	811.7	......	......
Dec. 3.....	1.992	212.3	211.2	582.0	580.1	813.2	......	......
Dec. 4.....	1.992	211.7	210.4	582.0	580.0	812.9	......	......
Mean ...	2.031	212.1	210.9	582.1	580.4	812.6	......	......

*In taking the means, the values marked with an asterisk have been omitted on account of their large deviation.

†Mean of experiments carried to 218°.

‡Mean of the two concordant determinations made in the U-shaped cell.

§Mean of experiments carried to 156°.

It will be seen from table 54 that the results of the separate experiments with sodium hydroxide agree closely with one another, very few of the initial values deviating from their mean by as much as 0.2 per cent. A comparison of the initial and final values at 18° shows that heating to 156° produced a decrease of conductance of less than 0.3 per cent in the three stronger solutions and one of 0.6 per cent in the 2 milli-normal solution, but that heating to 218° decreased it by 0.8 per cent in the 49 and 19 milli-normal and by 2.4 per cent in the 0.4 milli-normal. The latter decrease is so large that in deriving the best value at 218° we shall increase the mean value by half this amount or 1.2 per cent, it being probable that the observed decrease in conductance at 18° had taken place in some measure at 218°. At 18° with the 49 and 19 milli-normal solutions the mean results obtained in the U-shaped cell will be adopted as the best values, since these were not affected by polarization. In all other cases the mean of the initial values will be adopted.

Table 55 contains the results for ammonium chloride, which are derived from measurements with solutions of the salt containing about one-tenth as many equivalents of ammonium hydroxide (see table 53) by correcting the observed conductance for the conductance of the ionized portion of the base. In the case of the first two measurements (made on May 17), however, no free ammonia was added.

TABLE 55.—*Equivalent conductance of ammonium chloride at round temperatures.*

Date.	Concentration at 4°.	Equivalent conductance.				
		18°		100°		156°.
		Initial.	Final.	Initial.	Final.	
1905						
May 17...	12.492	121.49	......	......	......	......
May 17...	12.492	121.49	......	......	......	......
May 18...	12.513	121.65	121.72	379.5	......	569.1
May 19...	12.523	121.62	121.64	379.5	379.2	570.0
Mean ..	12.518	121.63	121.68	379.5	379.2	569.5
May 20...	1.9791	126.62	127.93	398.4	......	605.0
May 24...	2.076	126.53	127.65	399.4	401.8	605.1
Mean ..	2.027	126.57	127.79	398.9	401.8	605.0

The results of the separate experiments with ammonium chloride given in table 55 are in almost complete agreement. The two measurements of May 17 at 18°, made with the salt alone without the addition of ammonia, show that no considerable contamination resulted in the other cases from the presence of the base. A comparison of the initial and final values shows that no change in conductance was produced by the heating in the 12.5 milli-normal solution, but that there resulted from it an increase of 0.7 per cent at 100° and of 1.0 per cent at 18°. It has therefore seemed best to decrease the value at 156° at 2 milli-normal by 0.5 per cent in order to eliminate this effect as far as possible. This will be done in table 58 where the best values are brought together.

The initial and final values at 18° obtained with ammonium hydroxide (table 56) show that the heating had scarcely any effect on the 100 milli-normal solution, but that it caused a decrease of 0.7 per cent in the 33, and of 1 per cent in the 10-milli-normal solution. That this decrease, occurring in spite of the fact that almost any contaminating substance either by its own conductance or through salt-formation would produce an opposite effect, is due to destruction of the ammonia by oxidation, has been shown in connection with experiments made at 218° by Mr. R. B. Sosman in this laboratory, which will be later described. The effect in our experiments was fortunately not so great as to produce an important error, and it has seemed best not to attempt to correct for it, since contamination tends to compensate it.

TABLE 56.—*Equivalent conductance of ammonium hydroxide at round temperatures.*

Date.	No. of stock sol.	Concentration at 4°.	18° Initial.	18° Final.	100° Initial.	100° Final.	156°.
1905							
Feb. 9......	1	9.91	9.758	9.620	24.03	23.72	23.86
Feb. 10......	1		9.753	9.623	24.04	23.81	23.86
Feb. 27......	2	9.85	9.753†	9.668	23.86†	......	23.50†
Feb. 28......	2		9.759†	9.663	23.95†	23.79	23.55†
Jan. 13......	1	32.44	5.432†	......	13.302†	......	12.998†
Jan. 14......	1		5.425†	......	......	......	......
Jan. 16......	1		5.443	......	......	......	13.110
Jan. 17......	1	33.08	5.387†	5.251	13.185†	......	12.978†
Jan. 18......	1		5.391	5.347	13.223	......	13.010
Jan. 20......	1	33.07	5.385†	......	13.214†	......	12.952†
Jan. 21......	1		5.420	......	13.283	......	13.101
Jan. 27......	1	33.05	5.404†	......	13.284†	......	......
Jan. 28......	1		5.404	5.390	13.329	13.294	13.197
Jan. 30......	1		5.404	5.388	13.311	13.318	13.180
Feb. 25......	2	33.29	5.385†	5.370	13.196†	......	13.037†
Jan. 31......	1	97.07	3.171	3.166	7.845	7.837	7.748
Feb. 1......	1		3.171	3.177	7.871	7.891	7.861
Feb. 3......	1		3.177	3.178	7.876	7.890	7.865
Feb. 21......	2	99.90	3.106†	3.105	7.627†	......	7.490†
Feb. 23......	2		3.104†	3.103	7.643†	7.667	7.540†
Feb. 24......	2		3.104†	3.097	......	......	7.508†
			18°	51°	75.2°	100°	124.8°
Mar. 17......	3	102.59	3.062†	......	6.700†	7.521†	7.760†
Mar. 18......	3	102.59	3.061†	5.404	6.704†	7.520†	7.755†

The results show that in general lower values were obtained the fresher the solution, the differences being especially large at the highest temperature (156°). In deriving the most probable values, we shall therefore

TABLE 57.—*Equivalent conductance of ammonium hydroxide at uniform concentrations.*

Date.	No. of stock sol.	Concentration at 4°.	18°.	100°.	156°.
1905					
Feb. 21.......	2	99.90	3.106	7.627	7.490
Feb. 23.......	2		3.104	7.643	7.540
Feb. 24.......	2		3.104	......	7.508
May 17.......	3		3.101	7.622	......
May 18.......	3		3.100	7.621	......
Mean	..	99.90	3.103	7.628	7.513
Jan. 13.......	1	33.07	5.382	13.169	12.868
Jan. 17.......	1		5.387	13.185	12.978
Jan. 20.......	1		5.385	13.214	12.952
Jan. 27.......	1		5.404	13.284	......
Feb. 25.......	2		5.400	13.236	13.076
Mean	..	33.07	5.392	13.218	12.968
Feb. 27.......	2	9.853	9.753	23.86	23.50
Feb. 28.......	2		9.759	23.95	23.55
Mean	..	9.853	9.756	23.90	23.52

select the results obtained in the earlier measurements with each solution (those to which a dagger is attached in the table). In order to combine them, those at nearly the same concentrations have been reduced to a uniform concentration at 4° by means of the formula $\Lambda^2 C = \text{const.}$ As the agreement of the separate results can best be judged in this way, we give the so-obtained values in table 57. As the final values the mean of these will be adopted.

Table 58 contains what we regard as the best values which can be derived in the way stated in the preceding paragraphs from the summaries of the separate values given in tables 54, 55, and 57.

Table 58.—*Best values of the equivalent conductance at round temperatures.*

Concentration at 4°.	18°.	100°.	156°.	218°.
SODIUM HYDROXIDE.				
2.031	212.1	582.1	812.6	......
4.038	211.8	576.9	803.3	1008.8
21.55	205.5	......	......	......
19.151	......	560.6	774.1	941.7
50.31	200.6	......	......	......
49.08	......	542.7	745.3	891.6
AMMONIUM CHLORIDE.				
2.027	126.6	398.9	602.0	......
12.49	121.5	379.5	569.5	......
AMMONIUM HYDROXIDE.				
9.853	9.756	23.90	23.52	......
33.07	5.392	13.218	12.968	......
99.90	3.103	7.635	7.513	......

67. EQUIVALENT CONDUCTANCE AT ROUND CONCENTRATIONS.

The values given in table 58 refer to a different concentration at each temperature owing to the expansion of the solution. In order to show the effect of temperature alone they must be corrected to a uniform concentration at each temperature. This has been done with the values for sodium hydroxide and ammonium chloride by means of the empirical equation $\Lambda_1 - \Lambda_2 = K(C_2^{\frac{1}{3}} - C_1^{\frac{1}{3}})$, which states that the change of the equivalent conductance (Λ) at any one temperature is proportional to the change in the cube-root of the concentration ($C^{\frac{1}{3}}$); and with the values for ammonium hydroxide by means of the mass-action expression $\frac{\Lambda^2 C}{\Lambda_0 - \Lambda} = \text{const.}$ The results are given in table 59. Values extrapolated for a considerable interval are inclosed in parentheses.

TABLE 59.—*Equivalent conductance at round concentrations.*

Substance.	Concentration.	18°.	100°.	156°.	218.
Sodium hydroxide	0	(216.5)	(594)	(835)	(1060)
	2	212.1	582.0	813.5	......
	4	211.8	576.6	804.8	1003
	20	205.8	559.4	770.6	930
	40	......	......	746.0	889
	50	200.6	540.2	(738.2)	(873)
Ammonium chloride	0	(130.7)	(415)	(628)	......
	2	126.6	398.7	600.9	......
	11	......	380.7	570.4	......
	12.5	121.5	379.3	(567.1)	......
Ammonium acetate	0	(99.8)	(338)	(523)	......
	10	91.7	299.8	456	......
	25	88.2	286.5	426	......

Substance.	Concentration.	18°.	51°.	75.2°	100°.	124.8°	156°.
Ammonium hydroxide	0	(238)	(404)	(526)	(647)	(764)	(908)
	10	9.678	......	......	23.25	......	22.31
	30	5.656	......	......	13.58	......	12.99
	100	3.100	5.404	6.702	7.465	7.757	7.170

The values (Λ_0) for zero concentration or complete ionization have been calculated for ammonium chloride and for sodium hydroxide except at 218° by the graphical method which has been used throughout this series of investigations and is described in section 17, Part II. Since in the case of ammonium chloride the data did not suffice to determine the value of the exponent *n*, this was assumed to be the same as for potassium chloride, namely, 1.42. The results with sodium hydroxide at 218° are not accurate nor extensive enough to make this method reliable. The value of Λ_0 at 218° given in the table is an estimated one derived from the value of Λ_0 at the lower temperatures and from the corresponding Λ_0 values for sodium chloride and hydrochloric acid in the way described in section 84, Part VII.

The values of Λ_0 for ammonium hydroxide have been calculated by adding to the difference between the values for ammonium chloride and sodium chloride that for sodium hydroxide. The values for sodium chloride used were those given by Noyes and Coolidge, section 16, Part II, namely, 109.0 at 18°, 362 at 100° and 555 at 156°. The Λ_0 values for ammonium hydroxide at 51.0, 75.2 and 124.8° were interpolated graphically between those at the other three temperatures, and are less accurate than the values at the other temperatures. The concentrations are expressed in milli-equivalents per liter of solution.

The values given for ammonium acetate at 18° and 100° are based on the specific conductance values for the unhydrolyzed salt given below in table 67 under $\underline{L}_{BA}$. They have been corrected to round concentrations by means of the cube-root function. The values at 156° are similarly derived except that a correction was first applied by subtracting from the concentration of the salt (C_{BA}) that of the hydrolyzed portion still existing even in the presence of the largest quantity of added acid or base. The Λ_0 values are calculated from those for sodium acetate and chloride given in table 36, section 54, and those for ammonium chloride here given.

It is of some interest to compare the results at 18° with those obtained previously by Kohlrausch.* As far as the data are comparable they are placed side by side in the following table.

TABLE 60.—*Conductivity results of different investigators.*

Temperature.	Concentration.	Sodium hydroxide.		Ammonium chloride.		Ammonium hydroxide.	
		Noyes and Kato.	Kohlrausch.	Noyes and Kato.	Kohlrausch.	Noyes and Kato.	Kohlrausch.
18°	2	212.1	206	126.6	126.2	......	......
	4	211.8	204	......	......	......	......
	10	......	......	......	......	9.68	9.6
	12.5	......	......	121.5	121.3	......	......
	20	205.8	197	......	......	......	......
	30	......	......	......	......	5.66	5.8
	50	200.6	190	......	......	......	......
	100	......	......	......	......	3.10	3.3

The agreement of the ammonium chloride values is within about 0.3 per cent. Kohlrausch's values for sodium hydroxide, however, are 4 to 5 per cent lower than ours, and his value for ammonium hydroxide at 100 milli-normal is 6 per cent higher. As Kohlrausch's data are derived from his earlier measurements made in 1885, it is probable that the discrepancy arises from impurities in the substances or water used by him, especially since his values for potassium hydroxide (231 at 4 milli-normal, 219 at 50 milli-normal) after allowing for the difference in equivalent conductance of the potassium and sodium ions (21 or 19 units) accord within 1 per cent with ours for sodium hydroxide.

68. CHANGE OF THE EQUIVALENT CONDUCTANCE WITH THE CONCENTRATION AND TEMPERATURE.

With reference to the change of the conductivity with the concentration, we will limit ourselves to a consideration of the data for sodium hydroxide; for those with ammonium chloride and acetate do not cover a sufficient range of concentration.

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*See Kohlrausch and Holborn's Leitvermögen der Elektrolyte, pp. 159-160.

It may first be shown that this base, like the neutral salts, confor fairly closely at all temperatures to the simple cube-root formula of Ko rausch ($\Lambda_0 - \Lambda = KC^{\frac{1}{3}}$). Applying it in the form $\Lambda_{C_1} - \Lambda_{C_2} = K(C_2^{\frac{1}{3}} -$ $C_1^{\frac{1}{3}})$ we have first calculated the value of the constant K for $C_2 = 50$ (18° and 100°) or 40 (at 156° and 218°) and $C_1 = 4$, and have then calc lated the value of Λ_{C_1} for the intermediate concentration $C_2 = 20$. T percentage deviations of the so-calculated values from the observed valu given in table 59 are as follows: At 18°, +0.0; at 100°, —0.4; 156°, —0.3; and at 218°, +0.3. These deviations are not greater th the possible experimental errors.*

We have also determined graphically, by plotting $\frac{1}{\Lambda}$ against $(C\Lambda)^{n-1}$ described in section 17, Part II, what value of the exponent *n* in the fun tion $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$ best expresses the results with sodiu hydroxide at 18°, 100°, and 156°.† The values of *n* so determined a given in table 61. It will be seen that they correspond with the valu obtained for the neutral salts, all of which lie in the neighborhood of 1.

TABLE 61.—*Values of exponent n in the function* $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$.

Substance.	18°.	100°.	156°.
NaOH.....	1.50	1.50	1.50

The effect of temperature has interest especially with reference to t values at zero concentration; for in these the ionic velocities are alo involved. The mean temperature-coefficients ($\Delta\Lambda_0/\Delta t$) for sodium hydro ide and ammonium chloride are given in table 62.

TABLE 62.—*Mean temperature-coefficients of the equivalent conductance at zero concentration.*

Substance.	Equivalent Conductance at 18°.	Temperature-coefficient.		
		18°-100°.	100°-156°.	156°-218°.
NaOH....	215.8	4.60	4.30	3.63
NH_4Cl....	130.7	3.47	3.80	......

As in the case of hydrochloric acid (see section 55, Part V) the tempe ature-coefficient of sodium hydroxide decreases rapidly and steadily wi rising temperature, owing to a greatly decreased acceleration of the fast-moving ion. On the other hand with ammonium chloride, as with the other neutral salts previously investigated, the temperature-coefficient is greater between 100° and 156° than between 18° and 100°.

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*The values of the constant K when C is expressed in milli-equivalents per lit are 5.33 at 18°, 17.33 at 100°, 32.1 at 156°, and 61.9 at 218°. For purposes of inte polation they may be used with Λ values between $C = 4$ and $C = 50$, but not wi the Λ_0 values given in the table.

†Those at 218° are so affected by contamination in the more dilute and by pola zation in the more concentrated solution as to make a study of the concentrati function of little significance.

It is also of interest to note that with sodium hydroxide as with other substances the velocities of the ions approach equality with rising temperature. The ratios of the equivalent conductance at zero concentration to that of sodium chloride and potassium chloride (see section 54, Part V) at each temperature are as follows:

	18°	100°	156°	218°
NaOH : KCl	1.98	1.64	1.50	1.47
NaOH : NaCl	1.67	1.43	1.33	1.29

Finally, attention may be called to the fact that ammonium hydroxide like acetic acid at 0.1 to 0.01 normal exhibits a maximum of conductivity between 100° and 156° owing to the increase in migration-velocity being overcompensated by decrease in ionization.

69. IONIZATION VALUES AND THEIR CHANGE WITH THE CONCENTRATION AND TEMPERATURE.

The percentage ionization of the various substances is shown in table 63. The values were obtained by dividing the equivalent conductance at the different concentrations by that at zero concentration, as given in table 59. Those for 10-milli-normal sodium hydroxide were interpolated by

TABLE 63.—*Percentage ionization.*

Substance.	Concentration.	18°.	100°.	156°.	218°.
$NaOH$	0	100.0	100.0	100.0	100
	2	98.0	98.0	97.3	....
	4	97.9	97.0	96.3	95
	10	96.2	95.7	94.3	92
	20	94.9	94.1	92.3	88
	40	.....	.....	89.3	84
	50	92.5	90.9	(88.4)	(82)
NH_4Cl	0	100.0	100.0	100.0	....
	2	96.9	96.1	95.7	....
	10	93.7	92.2	91.2	....
	12.5	93.1	(91.4)	(90.3)	....
$NH_4C_2H_3O_2$...	0	100.0	100.0	100.0	....
	10	91.9	88.7	87.1	....
	20	.....	.....	83.0	....
	25	88.4	84.8	81.5	....

Substance.	Concentration.	18°.	51°.	75.2°.	100°.	124.8°.	156°.
NH_4OH	0	100.0	100.0	100.0	100.0	100.0	100.0
	10	4.07	.....	.....	3.59	.....	2.46
	30	2.38	.....	.....	2.10	.....	1.43
	100	1.31	1.34	1.27	1.15	1.02	0.79

means of the cube-root equation, so as to enable a comparison of this substance to be made with hydrochloric acid for which the results were presented in Part V.

It was shown in section 68 that the equivalent conductance Λ of sodium hydroxide changes with the concentration C in accordance with the expression $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$, where n is approximately 1.5, whence it follows that the ionization γ follows approximately the analogous law $C(1-\gamma) = K(C\gamma)^{1.5}$. Thus substantially the same relation between ionization and concentration holds true for this base as for hydrochloric acid and all the neutral salts thus far investigated.

That to ammonium hydroxide the mass-action law is applicable even at the higher temperatures is shown by the values of the ionization-constant $(C\gamma^2)/(1-\gamma)$ given in table 64. The concentration used in the calculation and given in the table is expressed in equivalents per liter and the constants have been multiplied by 10^6.

TABLE 64.—*Ionization-constants* ($\times 10^6$) *for ammonium hydroxide.*

Concentration.	18°.	51°.	75.2°.	100°.	124.8°.	156°.
0.01	17.3	......	......	13.4	......	6.20
0.03	17.4	......	......	13.5	......	6.24
0.10	17.2	18.1	16.4	13.5	10.4	6.28

The agreement is seen to be excellent. The last row of values at the highest concentration are the most reliable ones to adopt as final values of the constant.

The effect of temperature on the ionization-values will be seen from table 63. Those of sodium hydroxide like those of all other largely ionized substances investigated steadily decrease with rising temperature, and by about the same amount as with hydrochloric acid, whose percentage ionization at 10 milli-normal is 97.1 at 18°, 95.0 at 100°, 93.6 at 156°, and 92.2 at 218°. It is of some interest, too, to note, that ammonium acetate though a salt of both a weak acid and a weak base has about the same percentage ionization as sodium acetate, for which the values in 10 milli-normal solution are 91.2 at 18°, 88.8 at 100°, and 88.0 at 156°.

The ionization of ammonium hydroxide (table 63), and of course also its ionization-constant (table 64), increases slightly between 18° and 51°, which is in accordance with the fact that its ionization at 18° is attended with an absorption of heat of about 1,500 cal., since its heat of neutralization with hydrochloric acid is 12,200 cal. Above 100°, however, the ionization decreases rapidly, as with other substances.

70. DESCRIPTION OF THE HYDROLYSIS EXPERIMENTS.

As stated in section 60, the hydrolysis experiments were made by measuring the conductance of certain ammonium acetate solutions, containing in one case the salt alone and in other cases, in addition, varying quantities of ammonium hydroxide or acetic acid. Duplicate measurements were made at 18°, 100°, and 156° with acetate solutions of two concentrations, about 10 and 26 milli-normal. In the experiments with the mixtures, also made in duplicate, approximately equivalent, or two or five times equivalent, quantities of the base or acid were simultaneously present. The method of procedure in preparing the solution was to dilute quantitatively by weight the 50 milli-normal stock solution (see section 62) in one case with water and in other cases with the 100 milli-normal base or acid solution, enough water being also added in these cases to make the salt concentration the same as in the first case. The measurements were all made in the bomb in the usual way.

71. CONDUCTIVITY DATA FOR AMMONIUM ACETATE.

The data of the experiments with ammonium acetate alone and with acetic acid or ammonium hydroxide added are given in table 65 arranged as in the preceding tables (50-53); but the specific conductance has been given instead of the equivalent conductance, since we have to deal here with mixtures. This was calculated by correcting the observed conductance for that of the water (but only in the 10 milli-normal solutions since there it amounted to only about 0.1 per cent) and multiplying by the conductance-capacity. In the experiments with ammonium hydroxide added, made from March 27 to April 20, stock solution No. 3 prepared March 17 was used. In the later experiments of June 17 to June 26 an ammonium hydroxide solution freshly prepared (on June 17) was employed.

TABLE 65.—*Conductivity data for ammonium acetate.*

Date.	Concentration at 4°.		Temperature.	Conductance × 10^6.	Specific conductance × 10^6.
	$CH_3CO_2NH_4$.	NH_4OH.			
1905					
Mar. 24....	26.02	......	17.93	15,409	2,280
			100.08	46,250	6,838
			155.9	58,240	8,603
			17.93	15,373	2,275
Mar. 25....	26.02	......	17.93	15,413	2,281
			99.54	46,040	6,806
			155.6	58,410	8,629
			99.54	46,020	6,803
			17.93	15,396	2,278

TABLE 65.—*Conductivity data for ammonium acetate*—Continued.

Date.	Concentration at 4°.		Temperature.	Conductance × 10^6.	Specific conductance × 10^6.
	$CH_3CO_2NH_4$.	NH_4OH.			
1905					
Mar. 27....	26.06	51.21	17.93	15,543	2,300
			99.61	48,360	7,148
			155.6	69,160	10,215
			17.93	15,579	2,305
Mar. 28....	26.06	51.21	17.93	15,547	2,300
			99.84	48,540	7,175
			155.9	69,250	10,229
			99.84	48,520	7,172
			17.93	15,558	2,302
Mar. 29....	26.02	25.70	17.93	15,470	2,289
			99.92	48,380	7,151
			155.6	67,870	10,028
			17.93	15,473	2,290
Mar. 30.....	26.02	25.70	17.93	15,477	2,290
			99.74	48,280	7,137
			156.4	67,800	10,016
			99.75	48,280	7,137
			17.93	15,492	2,292
		CH_3CO_2H			
Apr. 5.....	25.99	26.47	17.93	15,458	2,287
			99.64	48,260	7,134
			156.0	66,890	9,881
			17.93	15,385	2,276
Apr. 6.....	25.99	26.47	17.93	15,461	2,288
			99.15	48,100	7,110
			155.7	67,070	9,907
			99.14	47,800	7,066
			17.93	15,420	2,282
Apr. 7.....	26.00	52.00	17.93	15,490	2,292
			99.49	48,280	7,138
			155.8	68,360	10,098
			99.50	48,030	7,100
			17.93	15,425	2,282
Apr. 8.....	26.00	52.82	17.93	15,480	2,290
			99.58	48,310	7,141
			155.6	68,300	10,090
			99.54	48,050	7,103
			17.93	15,437	2,284
Apr. 10.....	10.404	......	17.93	6,389	945.6
			99.49	19,235	2,843
			155.8	24,230	3,579
			99.45	19,159	2,832
			17.93	6,358	940.9
Apr. 11.....	10.404	......	17.93	6,392	945.9
			99.50	19,238	2,844
			156.1	24,260	3,584
			99.53	19,154	2,831
			17.93	6,368	942.4
		NH_4OH			
Apr. 12.....	10.410	10.263	17.93	6,452	954.2
			99.58	20,220	2,987
			156.0	28,390	4,190
			99.58	20,190	2,983
			17.93	6,478	951.0
Apr. 13.....	10.410	10.263	17.93	6,453	954.2
			99.65	20,250	2,992
			156.2	28,410	4,293

TABLE 65.—*Conductivity data for ammonium acetate*—Continued.

Date.	Concentration at 4°.		Temperature.	Conductance × 10^6.	Specific conductance × 10^6.
	$CH_3CO_2NH_4$.	NH_4OH.			
1905					
			99.62	20,210	2,986
			17.93	6,478	958.9
Apr. 14.....	10.405	20.52	17.93	6,488	959.4
			99.46	20,290	2,997
			155.9	29,070	4,292
			17.93	6,523	964.6
Apr. 15.....	10.405	20.52	17.93	6,495	960.5
			99.53	20,300	2,999
			156.2	29,070	4,292
			99.44	20,300	2,999
			17.93	6,519	963.9
Apr. 19.....	10.406	51.29	17.93	6,616	978.4
			99.81	20,580	3,040
			156.6	29,930	4,417
			17.93	6,650	983.4
Apr. 20.....	10.406	51.29	17.93	6,627	980.1
			99.69	20,600	3,042
			156.6	29,900	4,412
			99.69	20,610	3,044
			17.93	6,654	983.9
		CH_3CO_2H			
Apr. 21.....	10.407	21.12	17.93	6,514	963.3
			99.43	20,330	3,004
Apr. 24.....	10.406	52.76	17.93	6,641	982.4
			100.04	20,600	3,043
			......	......	......
			99.87	20,370	3,010
			17.93	6,607	977.0
Apr. 27.....	10.406	52.76	17.93	6,648	983.1
			155.8	29,230	4,316
			17.93	6,584	973.6
Apr. 29.....	10.407	21.13	17.93	6,509	962.5
			99.74	20,380	3,011
			155.7	28,730	4,241
			99.71	20,210	2,986
			17.93	6,480	958.1
May 2.....	10.409	10.569	17.93	6,469	956.6
			99.99	20,330	3,003
			156.0	28,260	4,170
			100.01	20,220	2,986
			17.93	6,448	953.8
May 3.....	10.425	10.577	17.93	6,482	958.7
			99.76	20,320	3,003
			155.4	28,250	4,169
			17.93	6,464	956.0
June 17....	10.321	50.12	17.93	6,538	966.8
			155.9	29,470	4,352
			17.93	6,549	968.3
June 21....	10.412	53.54	17.93	6,637	981.3
			99.88	20,670	3,054
			156.4	29,950	4,221
			17.93	6,677	987.4
June 26....	10.414	43.92	17.93	6,537	966.6
			99.29	20,470	3,025
			155.0	29,600	4,372
			17.93	6,595	975.1

72. SUMMARY OF THE SPECIFIC CONDUCTANCE VALUES.

Table 66 summarizes the values of the specific conductance corrected so as to correspond to round temperatures and to a uniform concentration of the salt. The correction to round temperatures was made with the help of temperature-coefficients obtained as in the previous cases. The correction to uniform concentration, which seldom exceeded 0.2 per cent, was made by assuming proportionality between it and specific conductance.

TABLE 66.—*Specific conductance of ammonium acetate solutions at round temperatures.*

Date.	Concentration at 4°.		Specific conductance × 10^6.				
			18°.		100°.		156°.
	$CH_3CO_2NH_4$.	CH_3CO_2H.	Initial.	Final.	Initial.	Final.	
1905							
Mar. 24	26.00	......	2,281	2,276	6,830	......	8,598
Mar. 25	26.00	......	2,282	2,279	6,821	6,816	8,632
Mean	26.00	......	2,281	2,277	6,825	6,816	8,615
Apr. 10	10.400	......	946.6	941.9	2,851	2,841	3,583
Apr. 11	10.400	......	946.9	943.4	2,852	2,839	3,581
Mean	10.400	......	946.7	942.6	2,851	2,840	3,582
Apr. 5	26.00	26.47	2,291	2,280	7,157	......	9,885
Apr. 6	26.00	26.47	2,292	2,286	7,158	7,114	9,925
Mean	26.00	26.47	2,291	2,283	7,157	7,114	9,905
Apr. 7	26.00	52.00	2,295	2,285	7,166	7,125	10,108
Apr. 8	26.00	52.00	2,293	2,287	7,164	7,128	10,109
Mean	26.00	52.00	2,294	2,286	7,165	7,126	10,108
Apr. 21	10.400	21.12	964.0	......	3,016	......	......
Apr. 29	10.400	21.13	963.2	958.8	3,015	2,991	4,243
Mean	10.400	21.13	963.6	958.8	3,015	2,991	4,243
Apr. 24	10.400	52.76	983.2	977.8	3,040	3,011	......
Apr. 27	10.400	52.76	983.9	974.4	......	......	4,318
Mean	10.400	52.76	983.5	976.1	3,040	3,011	4,318
May 2	10.400	10.569	957.1	954.3	3,000	2,983	4,166
May 3	10.400	10.577	957.7	955.0	3,002	......	4,170
Mean	10.400	10.573	957.4	954.6	3,001	2,983	4,168
		NH_4OH.					
Mar. 27	26.00	51.21	2,298	2,303	7,153	......	10,212
Mar. 28	26.00	51.21	2,298	2,300	7,168	7,164	10,211
Mean	26.00	51.21	2,298	2,301	7,160	7,164	10,211
Mar. 29	26.00	25.70	2,290	2,291	7,149	......	10,040
Mar. 30	26.00	25.70	2,291	2,293	7,145	7,145	9,988
Mean	26.00	25.70	2,290	2,292	7,147	7,145	10,014
Apr. 12	10.400	10.263	954.7	958.5	2,995	2,991	4,186
Apr. 13	10.400	10.263	954.7	958.4	2,998	2,992	4,185
Mean	10.400	10.263	954.7	958.4	2,996	2,991	4,185
Apr. 14	10.400	20.52	960.3	965.5	3,010	......	4,292
Apr. 15	10.400	20.52	961.4	964.8	3,010	3,013	4,286
Mean	10.400	20.52	960.8	965.1	3,010	3,013	4,289
Apr. 19	10.400	51.29	979.2	984.2	3,043	......	4,403
Apr. 20	10.400	51.29	980.9	984.4	3,048	3,050	4,398
June 17	10.400	50.12	976.1	977.6	......	......	4,388
June 21	10.400	53.54	981.6	987.7	3,053	......	4,408
June 26	10.400	*43.93	*966.8	*975.3	*3,036	......	*4,391
Mean	10.400	51.56	979.4	983.5	3,048	3,050	4,399

*Values with an asterisk were not included in deriving the mean.

It will be seen from these results that in case of the salt alone and of the mixture of it with acetic acid the final values both at 18° and 100° are from 0.2 to 0.9 per cent lower than the initial values at the same temperatures, showing that in the heating at 156° some change took place by which the conductance was decreased. On the other hand with the mixtures containing ammonia the final values do not differ much from the initial ones in the case of the 26 milli-normal solution, but are larger than the latter in the case of the 10 milli-normal one by about 0.4 per cent at 18° and by about 0.15 per cent at 100° showing that some contamination took place in heating to 100° and that this increased on heating to 156°.

The final data needed for the computation of the hydrolysis and some calculated values derived from them are presented in table 67. The first column gives the temperature, and the next two columns give the concentrations of the salt and acid or base in milli-equivalents per liter at that temperature. The column headed $\underline{L}_{\mathrm{M}}$ contains the most probable values of the specific conductance derivable from the separate values of table 66. At 18° the means of the "initial" values have been adopted; and the same is true at 100° in the case of the ammonium acetate alone and of the mixture of it with acetic acid. In the case of the mixtures with ammonia the mean initial values of the specific conductance were decreased by half the percentage amount at 100°, and by the same percentage amount at 156°, as the initial differed from the final conductance at 18°. At 156° in the case of the salt alone and the mixtures with acetic acid, the specific conductance was increased by the same percentage amount as the initial differed from the final conductance at 100°. These corrections are based upon the indications of contamination just referred to.

In the next column of the table under $\underline{L}_{\mathrm{HA}}$ or $\underline{L}_{\mathrm{BOH}}$ is given the conductance of the ammonium hydroxide or acetic acid present in the solution. This conductance has been calculated in the following manner: In the mass-action equation

$$\frac{C_{\mathrm{B}}C_{\mathrm{OH}}}{C_{\mathrm{BOH}}} = K_{\mathrm{B}} \text{ or } \frac{C_{\mathrm{A}}C_{\mathrm{H}}}{C_{\mathrm{HA}}} = K_{\mathrm{A}}$$

(where B represents the ammonium ion or radical and A the acetate ion or radical) we can substitute for C_{B} or C_{A} the ratio $\underline{L}_{\mathrm{BA}}/\Lambda_{0\mathrm{BA}}$ of the specific conductance ($\underline{L}_{\mathrm{BA}}$) of the salt to its equivalent conductance ($\Lambda_{0\mathrm{BA}}$) when completely ionized, and thus obtain in terms of known quantities C_{OH} or C_{H}, which is the concentration of the dissociated base or acid. Multiplying this by the equivalent conductance ($\Lambda_{0\mathrm{BOH}}$ or $\Lambda_{0\mathrm{HA}}$) of the base or acid when completely ionized, we get the specific conductance ($\underline{L}_{\mathrm{BOH}}$ of $\underline{L}_{\mathrm{HA}}$) of the base or acid in the mixture. That is: $\underline{L}_{\mathrm{BOH}} = K_{\mathrm{B}}C_{\mathrm{BOH}}\,\Lambda_{0\mathrm{BOH}}\frac{\Lambda_{0\mathrm{BA}}}{\underline{L}_{\mathrm{BA}}}$ and $\underline{L}_{\mathrm{HA}} = K_{\mathrm{A}}C_{\mathrm{HA}}\Lambda_{0\mathrm{HA}}\frac{\Lambda_{0\mathrm{BA}}}{\underline{L}_{\mathrm{BA}}}$. The values of $\Lambda_{0\mathrm{BA}}$ employed are those given in table 59.

The values so computed of $\underline{L}_{BOH}$ or $\underline{L}_{HA}$ have then been subtracted from the specific conductance $\underline{L}_{M}$ of the mixture and the resulting differences, which represent the specific conductance of the salt in the mixture, are given in the succeeding column headed $\underline{L}_{BA}$.

In the next to last column headed $\underline{L}_{B}$ is given the specific conductance of the salt when present in water alone at the same concentration which it has in the mixture, the values given at 18° and 100° being the mean of the directly observed initial values recorded in table 66, and those at 156° being the corresponding mean increased so as to correct for contamination as stated in the first paragraph of this section.

In the last column headed $\underline{L}_{BA} - \underline{L}_{B}$ is given the difference between the values in the two preceding columns. This difference represents the increase of conductance produced by reduction of the hydrolysis by the addition of the base or acid.

TABE 67.—*Specific conductance of constituents in ammonium acetate solutions.*

Temperature	Concentration at t°.		Specific conductance $\times 10^6$.				
	Salt.	Acid (A) or Base (B).	Mixture.	Acid or base in mixture.	Salt in mixture.	Salt alone in water.	Increase.
t°.	C_{BA}.	C_{HA} or C_{BOH}.	$\underline{L}_{M}$.	$\underline{L}_{HA}$ or $\underline{L}_{BOH}$.	$\underline{L}_{BA}$.	$\underline{L}_{B}$.	$\underline{L}_{BA}-\underline{L}_{B}$.
18	25.96	26.43 A	2,291	7	2,284	2,281	3
	25.96	25.66 B	2,290	4	2,286	2,281	5
	25.96	52.76 A	2,294	15	2,279	2,281	—2
	25.96	51.14 B	2,298	9	2,289	2,281	8
	....	....	......	Mean....	2,285	2,281	4
	10.387	10.559 A	957	7	950	947	3
	10.387	10.249 B	955	4	951	947	4
	10.387	21.09 A	964	14	950	947	3
	10.387	20.50 B	961	9	952	947	5
	10.387	52.69 A	983	35	948	947	1
	10.387	51.49 B	976	22	954	947	7
	....	....	......	Mean....	951	947	4
100	24.92	25.37 A	7,157	10	7,147	6,825	322
	24.92	24.63 B	7,144	9	7,135	6,825	310
	24.92	50.64 A	7,165	20	7,145	6,825	320
	24.92	49.09 B	7,156	19	7,137	6,825	312
	....	....	......	Mean....	7,141	6,825	316
	9.970	10.136 A	3,001	9	2,992	2,851	141
	9.970	9.838 B	2,990	9	2,981	2,851	130
	9.970	20.25 A	3,015	19	2,996	2,851	145
	9.970	19.675 B	3,003	19	2,984	2,851	133
	9.970	50.58 A	3,040	48	2,992	2,851	141
	9.970	49.43 B	3,041	47	2,994	2,851	143
	....	....	......	Mean....	2,990	2,851	139
156	23.68	24.11 A	9,964	5	9,959	8,625	1,334
	23.68	23.40 B	10,004	5	9,999	8,625	1,374
	23.68	48.12 A	10,163	13	10,150	8,625	1,525
	23.68	46.64 B	10,196	14	10,182	8,625	1,557
	9.473	9.631 A	4,193	6	4,187	3,596	591
	9.473	9.348 B	4,169	6	4,163	3,596	567
	9.473	19.243 A	4,278	13	4,265	3,596	669
	9.473	18.694 B	4,270	13	4,257	3,596	661
	9.473	48.06 A	4,360	31	4,329	3,596	733
	9.473	46.97 B	4,381	32	4,349	3,596	753

73. THE HYDROLYSIS OF AMMONIUM ACETATE AND THE IONIZATION-CONSTANT OF WATER.

From table 67 it will be seen that at 18° the excess of acid or base causes an increase of only 0.2 to 0.5 per cent in the conductance, in correspondence with the small degree of hydrolysis known to exist at this temperature. An accurate calculation of it from these results is therefore not possible. At the higher temperatures, however, the increase is considerable — about 5 per cent at 100°, and 15 to 21 per cent at 156°. At 100° the addition of a quantity of acid or base equivalent to the salt produced as great an increase as a larger quantity, showing that the hydrolysis had been reduced substantially to zero. The effect of the acid was, as it should be, nearly equal to that of the base, the small differences observed being doubtless due to experimental error. The percentage increase was also nearly the same at the two concentrations of the salt (4.6 and 4.9 per cent) respectively, showing that the hydrolysis does not increase much with the dilution, which is what the mass-action law requires for a salt whose acid and base are both weak. At 156° the second equivalent of acid or base produces a large further increase in conductance, showing that the salt is still somewhat hydrolyzed. Here again the acid and base have not far from the same effect, as they should have on account of the smallness of their ionization constants.

The quantitative calculation of the ionization at 100° is comparatively simple. Since the hydrolysis is reduced to zero by the added acid or base, the increase in specific conductance produced by it when divided by the equivalent conductance Λ_0 (338) of the completely ionized salt gives at once the number of equivalents per cubic centimeter of free acid and base which have been converted into ions. In addition a quantity of the un-ionized salt, corresponding to the increased concentration of its ions, is produced out of the acid and base. To compute this, we have made use of the equation $\frac{(C\gamma)^n}{C(1-\gamma-h)} = K$ (where γ is the fraction ionized and h the fraction hydrolyzed), in which we have determined the constants n and K from the conductances ($\underline{L}_{BA}$) of the unhydrolyzed salt (7,141 and $2,990 \times 10^{-6}$) at the two concentrations (24.92 and 9.97 milli-equivalents per liter) investigated and from the Λ_0 value for the salt.* We have then calculated from the values of $\underline{L}/\Lambda_0$, which are equal to $C\gamma$, the concentration of un-ionized salt, $C(1-\gamma-h)$, both in the solution containing the salt alone and in that to which acid or base had been added.

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*For this last calculation we used a preliminary value of Λ_0, namely 333 instead of 338; but this could have only an inappreciable influence on the result. The numerical equation so obtained when the concentration is expressed in milli-equivalents per liter is: $\log_{10} C(1-\gamma-h) = 1.443 \log_{10}(C\gamma) - 1.379$.

The excess of the second value over the first value gives the un-ionized salt, $\Lambda C(1-\gamma-h)$, that has been produced out of free acid and base: this added to the quantity $(\Delta C\gamma)$ of ions similarly produced gives the quantity of salt in the hydrolyzed state when it is alone present in water; and this divided by the concentration (C) gives the fraction hydrolyzed (h_0). The results of the computations are given in table 68.

TABLE 68.—*Hydrolysis of ammonium acetate and ionisation-constant of water at* 100°.

C	$100\gamma_0$ or $100\underline{\underline{L}}_s/C\Lambda_0$	$\Delta(C\gamma)$ or $(\underline{\underline{L}}_{BA}-\underline{\underline{L}}_s)/\Lambda_0$	$\Delta(C(1-\gamma-h))$	Ch_0	$100\ h_0$	$K_w \times 10^{14}$
24.92	82.2	0.94	0.21	1.15	4.61	48.5
9.97	85.9	0.411	0.064	0.475	4.76	47.4

It will be seen from table 68 that the hydrolysis h_0 is only a little greater at 10 than at 25 milli-normal. From each of these values the ionization-constant of water $(K_W = C_H \times C_{OH})$ has been calculated, and the results are given in the last column, the concentration being here expressed in equivalents per liter. The calculation was made by means of the mass-action expression $K_W = K_A K_B \frac{h^2}{\gamma^2}$ in which K_A and K_B are the ionization-constants of the acid and base respectively, and h and γ are the hydrolysis and ionization of the salt in water alone. This expression is readily obtained by multiplying together the two ionization-equations $K_A = \frac{C_H C_A}{C_{HA}}$ and $K_B = \frac{C_B C_{OH}}{C_{BOH}}$, substituting K_W for $C_H \times C_{OH}$, γC_S for C_A and for C_B, and $C_S h_0$ for C_{HA} and C_{BOH}, and transposing. It will be noted that the two independent values of K_W agree almost completely.

In order to calculate the hydrolysis at 156° from the conductance data it is necessary, since the hydrolysis is not reduced to zero even by the largest quantity of acid or base added, to unite with the empirical relation between the concentrations of ions and un-ionized molecules, the mass-action relation between the concentration of the ions and the products of the hydrolysis. These two expressions, if γ represents the fraction of the salt existing as ions and h the fraction hydrolyzed into free acid and base and C_S and C_{BOH} are the concentrations of the salt and of the added base (or acid) respectively, are

$$\frac{(\gamma C_S)^n}{C_S(1-\gamma-h)} = \text{const.} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

and

$$\frac{(\gamma C_S^2)}{(C_{BOH}+C_S h)C_S h} = \frac{\gamma^2}{\left(\frac{C_{BOH}}{C_S}+h\right)h} = \frac{K_A K_B}{K_W} = \text{const.} \quad \ldots\ldots (2)$$

Or, representing by γ_0 and h_0 the ionization and hydrolysis of the salt when in water alone, and by γ_1 and h_1 these same quantities when the concentration of the salt is the same, but base (or acid) is present in excess at a concentration C_{BOH}, and writing r for $C_{\mathrm{BOH}}/C_{\mathrm{S}}$ we have:

$$\left(\frac{\gamma_1}{\gamma_0}\right)^n = \frac{1-\gamma_1-h_1}{1-\gamma_0-h_0} \text{ (3) and } \left(\frac{\gamma_1}{\gamma_0}\right)^2 = \frac{h_1(r+h_1)}{h_0^2} \ldots\ldots\ldots (4)$$

two simultaneous equations which can be solved for h_0 and h since the other quantities may be derived from the measurements. Thus the ratio γ_1/γ_0 is equal to $\mathrm{L}_{\mathrm{BA}}/\mathrm{L}_{\mathrm{S}}$ (see table 67), and the separate values of γ_1 and γ_0 are given by the quotients $\mathrm{L}_{\mathrm{BA}}/C_{\mathrm{S}}\Lambda_0$ and $\mathrm{L}_{\mathrm{S}}/C_{\mathrm{S}}\Lambda_0$, Λ_0 being equal to 523. For the exponent n we assumed provisionally the value 1.5, which is that for sodium acetate at this temperature (see section 55, Part V); but after the hydrolysis had been computed for the two different salt-concentrations it was obtained by direct application of equation (1) to the mean of the two sets of results, and was thus found to be 1.45; and with this new value of n the calculations were repeated, although this variation in n produced a decrease in h_0 of only 0.7 per cent of its value both at 23.68 and at 9.473 milli-normal. Equations (3) and (4) can be completely solved algebraically for h_1 or h_0; but it is far simpler to use only the incomplete solution obtained by taking the logarithm of equation (3) and eliminating h_0 from it by means of equation (4), whereby results the expression:

$$\log \frac{1-\gamma_1-h_1}{(1-\gamma_0)\dfrac{\gamma_1}{\gamma_0}-\sqrt{h(r+h)}} = (n-1) \log \frac{\gamma_1}{\gamma_0}.$$

This equation can be readily solved for h_1 by trial, and h_0 can then be calculated by (4).

The results of the calculations are given in table 69. The headings will be understood by reference to the preceding paragraph. In computing the ionization-constant of water, which was done as before by the expression $K_{\mathrm{W}} = K_{\mathrm{A}}K_{\mathrm{B}} \dfrac{h_0^2}{\gamma_0^2}$, the concentration was expressed in equivalents per liter and the values of K_{A} and K_{B} used were 5.67×10^{-6} and 6.28×10^{-6} respectively. The letter A after the value of the ratio $r (= C_{\mathrm{S}}/C_{\mathrm{B}})$ signifies that acetic acid, the letter B, that ammonium hydroxide was present in excess.

TABLE 69.—*Hydrolysis of ammonium acetate and ionization-constant of water at 156°.*

C_s	r	$100\gamma_0$	100γ	$100\,h$	$100\,h_0$	$K_W \times 10^{14}$
23.68	1.018 A	70.73	81.66	3.95	17.6	221 A
23.68	0.988 B	70.73	81.99	4.34	18.2	236 B
23.68	2.032 A	70.73	83.23	2.13	17.8	225 A
23.68	1.969 B	70.73	83.49	2.46	18.3	238 B
Mean...	....	70.73	......	......	17.97	223 A 237 B
9.473	1.017 A	73.71	85.82	4.40	18.5	224 A
9.473	0.987 B	73.71	85.33	4.16	17.8	208 B
9.473	2.031 A	73.71	87.42	2.30	18.3	219 A
9.473	1.973 B	73.71	87.26	2.33	18.2	217 B
9.473	5.073 A	73.71	88.73	1.00	18.6	226 A
9.473	4.958 B	73.71	89.14	1.06	19.0	236 B
Mean...	....	73.71	......	......	18.60	223 A 221 B

An examination of the values of K_W given in the last column of table 69 shows that those derived from the experiments where acetic acid was added agree closely with one another not only in case of the successive additions of the acid but also at the two different concentrations of the salt; while those from the experiments where ammonium hydroxide was added are far less concordant whether considered with respect to the successive additions (in the second series) or to the different salt-concentrations. This fact, taken in conjunction with the experience that the base solutions are far more liable to contamination, justifies the adoption of the value 223×10^{-14} derived from the experiments with the acid as the best final value for the ionization-constant of water at 156°. It is worthy of note, however, that the mean value 229×10^{-14} derived from the experiments with the base is less than 3 per cent higher than this.

TABLE 70.—*Ionization of water at various temperatures.*

Temperature.	$K_W \times 10^{14}$	$C_H \times 10^7$
18	0.6	0.8
100	48	7.0
156	223	14.9

Finally it is of much interest to compare the values of the ionization-constants of water and the concentration of hydrogen or hydroxide ions in it at 18°, 100°, and 156°. At 18° the constant has been derived from the conductivity measurements of Kohlrausch and Heydweiller with the purest water obtainable, and this value has been roughly confirmed in a variety of other ways.* This we have included with our values at 100°

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*See Nernst, Theoretische Chemie, 4te Auflage, p. 503 (1903).

and 156° in table 70. The table also contains the concentration of the hydrogen or hydroxide ion ($C_M = C_{OH} = \sqrt{K_W}$) at all these temperatures.

It will be seen that the ionization-constant increases about 80-fold between 18° and 100°, but only 4½-fold between 100° and 156°. When it is considered that at these higher temperatures not only the ionization-constant of water is so much greater than at 18°, but also that the ionization of weak acids and bases is very much less than at 18°, it will be evident that the tendency of salts to hydrolyze is enormously increased at high temperatures. This is well illustrated by ammonium acetate itself, which at 0.01 normal concentration is hydrolyzed to an extent of 0.4 per cent* at 18°, 4.8 per cent at 100°, and 18.3 per cent at 156°.

74. SUMMARY.

In this article have been presented the results of conductivity measurements at various concentrations with sodium hydroxide at 18°, 100°, 156°, and 218°, with ammonium chloride and hydroxide at 18°, 100°, and 156°, and with ammonium acetate both alone and in the presence of an excess of ammonium hydroxide and acetic acid, at these same temperatures. For the final results see tables 59 and 67. From them the equivalent conductance at zero concentration has been derived by extrapolation or by the law of the independent migration of ions, and the ionization of all these substances has been calculated (see table 63). An indirect method of measuring and computing the hydrolysis of a salt of a weak acid and base from its conductivity alone and in the presence of free acid or base has been described (in section 73), and the method has been applied to the results with ammonium acetate. From the hydrolysis of this salt and the ionization-constants of ammonium hydroxide and acetic acid, the ionization of water at 100° and 156° has been calculated.

The results justify the following conclusions:

(1) The equivalent conductance of sodium hydroxide at zero concentration increases with rising temperature at a steadily decreasing rate as in the case of hydrochloric acid, and the ratio of it to that of sodium chloride approaches unity, showing that the hydroxide ion has a velocity more nearly equal to that of the chlorine ion at the higher temperatures.

(2) The degree of ionization of sodium hydroxide at all temperatures, the law of its change with the concentration, and its decrease with the temperature, all correspond closely to that of neutral salts of the same ionic type.

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*The value at 18° is calculated from the ionization-constants of water, acetic acid, and ammonium hydroxide.

(3) The degree of ionization of ammonium hydroxide increases slightly between 18° and 51°, but above 51° it decreases rapidly, as in the case of all other substances thus far investigated. Thus the values of its ionization-constant multiplied by 10^6 is 17.2 at 18°, 18.1 at 51°, 13.5 at 100°, and 6.3 at 156°. The mass-action law expresses the change with the concentration at all temperatures.

(4) The hydrolysis of ammonium acetate which is about 0.4 per cent at 18°, was found to be about 4.8 per cent at 100° and about 18 per cent at 156°, and to vary only slightly with the concentration of the salt, as the mass-action requires in the case of a salt of this type.

(5) The ionization-constant of water (that is, the product of the concentrations of the hydrogen and hydroxide ions in it) which has been previously found by Kohlrausch and Heydweiller to be 0.6×10^{-14} at 18, is 48×10^{-14} at 100°, and 223×10^{-14} at 156°, as deduced from the hydrolysis of ammonium acetate. This great increase combined with the decrease in ionization of weak acids and bases produces at high temperatures an enormous increase in the tendency of salts to hydrolyze.

PART VII.

CONDUCTIVITY AND IONIZATION OF AMMONIUM HYDROXIDE, AMMONIUM CHLORIDE, AND ACETIC ACID AT 218° AND 306°, AND OF SODIUM ACETATE AT 306°. HYDROLYSIS OF AMMONIUM ACETATE AND IONIZATION OF WATER AT 218° AND 306°.

BY ROBERT B. SOSMAN.

PART VII.

CONDUCTIVITY AND IONIZATION OF AMMONIUM HYDROXIDE, AMMONIUM CHLORIDE, AND ACETIC ACID AT 218° AND 306°, AND OF SODIUM ACETATE AT 306°. HYDROLYSIS OF AMMONIUM ACETATE AND IONIZATION OF WATER AT 218° AND 306°.

75. OUTLINE OF THE INVESTIGATION.

This investigation is substantially an extension to higher temperatures of the investigation of Noyes and Kato (see Part VI) on the hydrolysis of ammonium acetate and the ionization of water at 100° and 156°. Noyes and Cooper (see Part V) have, to be sure, determined roughly the ionization of water at 218° from the hydrolysis of sodium acetate; but, on account of the small degree of hydrolysis, the probable error in their calculation is large. It was the object, therefore, of the present investigation to derive as accurately as possible the value of the ionization of water at 218° and at 306° from the hydrolysis of ammonium acetate. The experimental data necessary are: the conductivities at 218° and 306°, at small concentrations, of sodium chloride, sodium acetate, hydrochloric acid, sodium hydroxide, and ammonium chloride; the conductivities of ammonium hydroxide and acetic acid at varying concentrations; and the conductivity of ammonium acetate alone and with varying additions of ammonium hydroxide or acetic acid. Of these, the data at 218° for the first three substances and for acetic acid have been determined by Noyes and Cooper; those for sodium hydroxide at 218°, by Noyes and Kato; those for sodium chloride at 306°, by Noyes, Coolidge, and Melcher; and those for hydrochloric acid at 306°, by G. W. Eastman. The data for sodium hydroxide at 306° have not yet been determined, but an estimate of its equivalent conductance for complete ionization has been made on the basis of the results at lower temperatures and the relations to the conductance of the other substances.

76. APPARATUS AND PROCEDURE.

The apparatus employed was in principle the same as that used in the previous high-temperature investigations. The conductivity cell or bomb, the details of which have been fully described in Part II, was a new one (No. 4) made in June, 1904.* An open cylindrical platinum-iridium electrode was used as in the work of Noyes and Kato.

For the purpose of merely testing solutions at 18°, when it was not desired to make a measurement at higher temperatures, a small glass conductivity-cell was used, such as is represented in figure 19, Part IX. This had a capacity of about 40 c.cm., and was in the form of an ordinary pipette; the upper tube was provided with a stopcock, the platinum electrodes were sealed in vertically through the shoulder of the bulb on opposite sides of the upper tube, connection being made through glass tubes containing mercury, and the lower exit tube was turned upwards, so as to rise above the liquid in the temperature bath. Solutions could be forced into this cell without any danger of contamination from the air.

The resistance of the solution in the bomb was measured by means of the usual arrangement, consisting of a new Kohlrausch three-meter cylindrical slide-wire bridge (Hartmann and Braun No. 283), a small induction coil, and a telephone connected between the ends of the slide-wire. A switch was arranged to commutate the current from the coil, and another to connect the bridge with the lower or the upper electrode. The leads were of heavy copper wire, connecting with the bridge or with the leads coming out of the temperature bath by means of double flexible lampcord and flat binding-screws.

The rotating carriage in which the bomb was mounted, as well as the larger temperature baths required by this rotating arrangement, were similar to those used by Noyes and Melcher (section 28, Part III). Xyene was used in the 18° bath, and naphthalene in the 218° vapor bath. A Beckmann thermometer was used in each. In the 306° bath benzophenone was employed. Diphenylamine, boiling at 302°, was used at first, and some of the data on ammonium hydroxide were obtained at this temperature; but after a few experiments much of the substance had decomposed, and the boiling-point rose and became uncertain. It was found impracticable to use a Beckmann thermometer at this temperature, because its readings were variable and not reproducible. A 0 — 360° Alvergniat thermometer, graduated in degrees, was therefore employed.

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*This bomb was used until June 5, 1906, when the lining of it cracked; after this date another bomb (No. 3) was employed. The first trouble from leakage occurred in February, 1905, after the bomb had been in use for one month, when the lower lining cracked near the bottom; this was repaired by removing the lining and flowing gold over the crack. No more difficulty was experienced, except from occasional accidental leakage at the electrodes or the valve, until after the first heating to 302°, when a slow leak developed through a tear in the lining of the upper chamber, caused probably by unequal expansion of the steel and the platinum lining. The leak was so slow at first, however, that the conductivity of the ammonium hydroxide solution could be determined at a given time, and the bomb then removed and cooled without further loss, the solution from the bomb being always analyzed after each heating, whether there had been leakage or not. After some attempts to locate and repair this leak, the upper lining was removed and a new one put in (March, 1906). The bomb then held until June 5, when the lower lining again cracked.

To prevent contamination of the solutions by carbon dioxide or other gases in the air, they were kept in closed bottles, and blown out through an exit tube by means of compressed air which was purified by passing through a train of bulbs containing sulphuric acid and potassium hydroxide solutions. In filling the bomb, a procedure similar to that of Noyes and Kato was followed; and the results show that appreciable contamination by carbon dioxide was excluded. After the bomb was closed, the air was exhausted by means of a water-jet pump or a mechanical vacuum pump (see also section 79). The residual pressure was read on a mercury vacuum-gage.

The bomb in its carriage was then placed in the 18° bath and rotated until the resistance became constant, after which nine readings were taken, three on each of three known resistances, such as 101, 110, and 1,000 ohms. The 218° bath had meanwhile been heated and the naphthalene brought to boiling. The vapor was temporarily condensed by the air cooling-coil, the bomb and carriage introduced, and the naphthalene again boiled until the Beckmann thermometer showed a constant temperature nearly equal to the boiling-point of pure naphthalene at the prevailing atmospheric pressure. At the same time the resistance of the upper electrode was measured, showing how full the bomb had become and also showing whether any leakage was taking place. After the nine readings of resistance were made at 218°, the vapor was condensed, and the bomb removed and cooled to room temperature before a fan. The measurement at 18° was then repeated to find out whether any change had occurred in the solution. The same procedure was followed at 306°, except that, in order to avoid loss of benzophenone, the bath was not heated before introducing the bomb. The experiments at 306° were all made after the work at 218° had been completed.

The temperature in the 18° bath was kept constant within 0.01°, and was measured with a Beckmann thermometer. This was compared at various points in the neighborhood of 18° with a Baudin thermometer (No. 15958) which had been standardized by the Bureau of Standards at Washington. The corrected temperatures of the standard are referred to the hydrogen thermometer. At 218° the difference in temperature between the vapor-bath and a calibrating bath containing pure naphthalene was determined by means of a Beckmann thermometer.

The naphthalene used in the calibrating bath was obtained by recrystallizing the purest Kahlbaum preparation once from absolute alcohol; that the original substance is pure is shown by the fact that the recrystallized material did not differ more than 0.01° from the original in boiling-point. The 218° point on the Beckmann thermometer was determined in the calibrating bath after every second heating by reference to the known boiling point of naphthalene under the corrected atmospheric pressure as determined by a mercurial barometer. The 306° point on the Alvergniat thermometer was frequently determined by heating it in a calibrating bath containing pure benzophenone, prepared by crystallizing a Kahlbaum preparation from absolute alcohol. For the boiling-points of both naphthalene and benzophenone the values on the hydrogen thermometer determined by Jaquerod and Wassmer* were employed.

77. INSTRUMENTAL ERRORS AND THEIR CORRECTIONS.

There was no appreciable inaccuracy in the temperature measurement at 18°; and at 218° and 306° the measurement certainly gave the true temperature of the bomb within 0.2°. An uncertainty of 0.1° in temperature at 218° corresponds in the worst case to less than 0.1 per cent in the conductance, as the temperature-coefficient at this point is always less than 1 per cent. At 306°, 0.1° corresponds at the maximum to about 0.3 per cent. No variation was, however, noticeable in the conductance after it had reached its final value, so that the error, if any, is probably all in the temperature value.

The slide-wire was calibrated three times by the method of Strouhal and Barus: once by division into ten parts, and twice by division into twenty parts. The results agreed within 0.1 mm., and the correction was at no point greater than 0.2 mm. The 1, 10, and 100 ohm coils of the rheostat were compared, on a Carey-Foster bridge, with the Reichsanstalt standards in the Electrical Department of this Institute of Technology. The 1,000 and 10,000 ohm coils were tested by making up a Wheatstone system, using two standards as ratio arms and a third as known resistance, adjustment being made on the slide-wire of the Carey-Foster bridge. The maximum error found was 0.15 per cent, in the 1-ohm coil.

The measured resistance includes the resistance of the leads from the bridge to the bomb. This was measured by the drop-of-potential method, the bomb being placed in position as usual, except that the lower electrode tag was wired tightly against a polished spot on the bomb itself. To the resistance thus measured must be added, first the increase due to the heating of the leads inside of the bath, which was calculated from the size and temperature-coefficient of the copper wire, and second, the resistance of the stem of the electrode. The latter is, however, only 0.002 ohm. The maximum lead resistance was 0.034 ohm, at 306°, while the lowest total resistance measured was 19 ohms. The only possibility of variation in the lead resistance was at the removable contacts between electrode tag and electrode, bomb and carriage, carriage and supports, and the outside flexi-

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*J. chim. phys., **2**, 52 (1904).

ble leads and the main leads. All of these surfaces were polished with fine sandpaper before each heating. Special experiments showed that the brass contact surfaces are almost unaffected by tarnishing, but that the steel surface resistances are increased appreciably by a film of oxide; also that the variation in resistance at the sliding contact of the carriage on its supports is inappreciable.

The current used in the measurements was made as small as possible, so as to avoid the ejection from the electrode of adsorbed material. This was accomplished by using the smallest possible voltage on the coil, after weakening its spring by filing partly through it. Any error from polarization caused by asymmetry of the coil, was eliminated by commutating the current and taking the mean of the two readings.

The excess of pressure due to air in the bomb was only a small fraction of the total pressure; for instance, if the air is evacuated before the heating down to a pressure of 2 cm. of mercury, and the vapor-space at 218° is 2 c.cm., then the air pressure at 218° is 0.5 atmosphere, while the vapor-pressure is about 22 atmospheres. With 2 c.cm. vapor-space at 306°, the air pressure is about 1 atmosphere, while the vapor-pressure is about 97 atmospheres.* Hence the variation in conductivity due to the residual air pressure is probably negligible.

Down to the lowest level ordinarily used, namely with the bomb three-quarters full, the height of the solution in the bomb has no effect on the conductance-capacity. In the experiments for determining the vaporization-correction at 306°, however, the bomb was only half full at 18°; the effect on the conductance-capacity was determined by filling the bomb only to this level with a standard potassium chloride solution. The results are given in section 81. The correction for the variation in conductance-capacity with the temperature was made as described in section 36, Part IV.

78. PREPARATION OF THE SUBSTANCES AND SOLUTIONS.

The weights used in weighing out the solid substances and solutions were all standardized in terms of the one-gram weight as standard. All weights were reduced to weights in a vacuum before being used in calculations. The atomic weights used were those reported by the International Committee in 1904, referred to oxygen as 16.00.

All solutions both strong and dilute, except those used for determining the conductance-capacities of the apparatus, were made up, analyzed, or titrated wholly by weight; the results are therefore independent of temperature, and are expressed in terms of milli-equivalents per kilogram of solution. All of the dilute solutions were diluted in a weighed 500 c.cm. flask, provided with a stopcock and delivery tube, and were forced in or out by purified air. All flasks and bottles used for making or keeping solutions were steamed out for several days, after standing for some time filled with a dilute alkali solution.

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*Batelli, Landolt-Börnstein-Meyerhoffer Tabellen, p. 122 (1905).

The water was made by redistilling ordinary distilled water, after adding to it alkaline permanganate which had been previously boiled. It was distilled from a steam-jacketed copper still, and condensed hot in a tin condenser, a large part being allowed to pass away as steam. It was collected only in two- or four-liter hard glass "Non-Sol" bottles furnished by Whitall, Tatum & Co., and allowed to cool in these, as hot water dissolves ordinary glass appreciably. The first and last portions of the distillate were rejected. No water of specific conductance greater than 0.9×10^{-6} at 18° was used in making up the solutions.

The salts used for determining the conductance-capacity were sodium and potassium chlorides and potassium nitrate. The sodium chloride was made by precipitating Baker and Adamson "C. P." salt twice with hydrochloric acid gas. The potassium chloride was made by precipitating the "C. P." salt furnished by Baker and Adamson with hydrochloric acid gas, and crystallizing from hot water. The potassium nitrate was made by twice recrystallizing "C. P." salt from the same source. The salt gave no test for sulphate or chloride.

In preparing the solutions, the sodium and potassium chlorides were ignited in a platinum dish, the potassium nitrate dried at 130° to constant weight; the proper quantity of salt was weighed out and dissolved in a 2-liter flask, and the solution then diluted to the mark. The conductance of a sample of the water used was tested at the same time. A fresh solution was made for every determination.

Ten liters of an approximately 0.1 normal solution of hydrochloric acid were prepared from strong "chemically pure" acid, as a titration standard.* This was analyzed by precipitation with silver nitrate, and by titration against a solution of sodium carbonate. prepared from pure sodium bicarbonate, using methyl orange as indicator. The acidity determination was practically identical with the chlorine determination. The value used was 90.46 milli-equivalents per kilogram of solution.†

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*50 c.cm. of the strong acid were evaporated to dryness on a steam-bath; the residue was organic, and amounted to only 0.01 per cent of the total hydrochloric acid. 30 c.cm., evaporated with barium chloride, gave no test for sulphate. The water used in diluting it had at 18° a conductance less than 1.4×10^{-6}.

†Derived from the following data:

Grams of solution..................	93.84	104.70	105.98	126.59
Grams AgCl	1.2169	1.3579	1.3748	1.6425
Milli-equivalents HCl per kilogram...	90.44	90.45	90.47	90.49

Mean.......90.46. Average deviation = 0.02 per cent. By titration of Na_2CO_3..90.43.

A barium hydroxide solution was prepared for the purpose of titrating acetic acid solutions. This was found by titration against the standard hydrochloric acid, using phenolphthalein and excluding carbon dioxide, to have 80.73 milli-equivalents per kilogram of solution.*

The ammonia solutions were from two independent sources: first, a special preparation of specific gravity 0.90, obtained from Baker and Adamson, marked "free from amines, carbonate, and silicate"; second, redistilled liquid ammonia. The solutions were made by filling a 6-liter bottle with conductivity-water, displacing this completely with pure air, then forcing in water of conductance less than 0.9×10^{-6}. When the strong ammonia solution was used, it was introduced by means of a pipette, under the surface of the water. When liquid ammonia was employed, it was first drawn off into an iron cylinder and allowed to stand in contact with metallic sodium for several weeks. From this cylinder it was distilled, passing through plugs of asbestos into a small glass bulb from which the air had been previously evacuated; this bulb stood in a tube of liquid ammonia, which was kept rapidly evaporating by a current of air over the surface of the liquid. The ammonia within the bulb was thus condensed until the proper quantity was obtained (about 15 c.cm.); the air current was then stopped, the ammonia surrounding the bulb partly removed, and the pure ammonia within was allowed to distill through a plug of cotton directly into the water, through the exit tube of the bottle. The last cubic centimeter was rejected. A procedure adopted later consisted in distilling the ammonia from the iron cylinder into a flask containing solid ammonium nitrate, and kept in a freezing mixture. The nitrate readily absorbs its own weight of ammonia, and the mixture has a relatively low vapor pressure, so that the ammonia could be preserved in the flask, which was closed by a glass stopcock, and could be redistilled therefrom at room temperature when needed.

The concentration was determined by titrating the standard hydrochloric acid with the ammonia, using as indicator at first phenacetolin, and later Congo red, both of which gave a better end-point than methyl orange. The solutions could not be kept long, as they began to increase in conductance after about three weeks, probably because of action on the glass, and they were not considered trustworthy after the conductance had risen 0.2 per cent. The following list gives the date of making the stock solutions, and the source from which the ammonia was obtained; the number corresponds to that in section 82.

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*Derived from the following data:

Grams HCl solution	70.25	82.88	74.36
Grams $Ba(OH)_2$ solution	78.76	92.89	83.36
Milli-equivalents per kilogram	80.74	80.76	80.68

(1) February 30, 1905. Same as stock solution No. 2 of Noyes and Kato (see Part VI).
(2) April 11. From Baker and Adamson's aqua ammonia used by Noyes and Kato.
(3) June 8. From a new supply of Baker and Adamson's aqua ammonia.
(4) June 10, and (5) June 16. From liquid ammonia.
(6) June 24. From same supply as No. 3.
(7) July 19, (8) October 16, and (9) November 2. From liquid ammonia.
(10) February 2, 1906, and (11) February 19. From liquid ammonia distilled from ammonium nitrate.
(12) March 3. From a new supply of Baker and Adamson's aqua ammonia.
(13) May 22. From same supply as No. 11.

The acetic acid was made from a preparation of Kahlbaum, marked "99 – 100 per cent." This was twice fractionated by freezing, and once distilled, the yield being 200 grams out of 625. The distillate was received in three fractions. Solutions Nos. 1 and 2 (July 14, 1905) were made from the second and third fractions respectively. No. 3 (July 18) was from the same acid as No. 2, redistilled once. Nos. 4 (October 9, 1905) and 5 (May 6, 1906) were from the same acid as No. 1, redistilled twice. No. 6 (May 12, 1906) was made from a new supply of the Kahlbaum acid, redistilled three times, the portion used distilling at 117.7° to 118.0°. The concentration was determined by titrating the standard barium hydroxide with the acid, using phenolphthalein as indicator and excluding carbon dioxide.

The ammonium acetate solutions were made by mixing weighed quantities of the ammonium hydroxide and acetic acid solutions in such proportion as to form a neutral solution. Large enough quantities were taken to make the error of weighing negligible. Solution No. 1 was made from ammonia No. 7 and acid No. 3; No. 2, from ammonia No. 8 and acid No. 4. The same solutions were used in adding an excess of acid or base as were used in making the neutral salt solution, except in the experiments following Expt. No. 2.18; in these, acid solutions Nos. 5 and 6, and ammonia solution No. 13 were used.

The ammonium chloride was made by first subliming Baker and Adamson "C. P." salt, "free from traces of hydrocarbons," then recrystallizing this salt three times. Part of the salt was dissolved in water of specific conductance 0.8×10^{-6}, and the concentration of this solution (No. 1) found by precipitation with silver nitrate to be 100.8 milli-equivalents per kilogram.* For comparison, solution No. 2 was made by mixing the proper quantities of standard hydrochloric acid and ammonia No. 9.

The sodium acetate was made by recrystallizing J. T. Baker's "C. P." analyzed preparation, the analysis being given as "no iron or other metals,

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*Derived from the following data:

Grams of solution..............	109.29	113.07	121.24
Grams AgCl	1.5800	1.6337	1.7518
Milli-equivalents per kilogram....	100.83	100.77	100.77

no sulphates, 0.0006 per cent Cl." The recrystallized salt was dissolved in water of specific conductance 1.1×10^{-6}, and the concentration of the solution was found, by evaporation with pure hydrochloric acid and gentle ignition to constant weight, to be 112.2 milli-equivalents per kilogram.*

79. ERRORS AFFECTING THE SOLUTIONS AND THEIR CORRECTION.

The effect of carbon dioxide on the conductivity of ammonium hydroxide solutions can be shown to be very large. Thus, the ammonium carbonate formed by the addition of 0.01 per cent (in mols) of carbon dioxide to a 0.1 molal ammonium hydroxide solution is not appreciably hydrolized, on account of the large excess of ammonia present; considering it therefore as being completely ionized, and taking the equivalent conductances of NH_4 and CO_3 as 64 and 70 respectively, the increase in the specific conductance of the 0.1 molal ammonia solution, caused by the addition of the carbon dioxide, is found to be 2.7×10^{-6}, or 0.9 per cent of that of the ammonium hydroxide. That even such a small amount, which would of course vary considerably, was not absorbed during the filling of the bomb, is shown by the fact that successive determinations of the resistance of the same solution agree at 18° within 0.1 per cent.

The error due to carbon dioxide in the water used for making the solution or in the strong ammonia solution itself, is almost impossible to determine. Water at 17° absorbs its own volume of carbon dioxide at atmospheric pressure; ordinary air contains about 0.04 per cent CO_2 by volume, hence water in equilibrium with ordinary air will contain 17×10^{-6} mols of un-ionized H_2CO_3 per liter. Using Walker's† value of 3040×10^{-10} for the ionization-constant of H_2CO_3 into H^+ and HCO_3^-, and taking for the equivalent conductances of these ions 320 and 50, respectively, the specific conductance of this water should be 0.8×10^{-6}. The specific conductance of the water actually used was always less than 1.0×10^{-6}, usually less than 0.8×10^{-6}; but it is very unlikely that this water was saturated, since it was condensed hot, and afterward kept protected from the air. Hence the larger part of the conductance found was probably due to organic bases which distil over with the water, or to salts carried over mechanically by the current of steam. The view that it is not due to carbonic acid is supported by the fact that ammonium hydroxide solutions made from water varying in conductance from 0.5×10^{-6} to 0.8×10^{-6} show, after subtracting the conductance of the water, values for the equivalent conductance constant

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*Derived from the following data:

Grams of solution	114.97	118.84	120.42
Grams NaCl	0.7540	0.7799	0.7916
Milli-equivalents per kilogram	112.10	112.18	112.37

†Z. phys. Chem., **32**, 137 (1900).

within 0.1 per cent. Samples of the water, after being heated to 218° or 306°, showed an increased conductance at 18°, and were not changed by further heating, indicating the presence of a small amount of some organic substance, which was decomposed or oxidized at the high temperatures.

If originally present in the strong ammonium hydroxide solution from which the diluter solution was made, carbon dioxide of course would have the same effect as if present in the water, in giving too high a value. In fact, practically any imaginable impurity in the strong solution would have the effect of increasing the conductance, so that the lowest value obtained should be considered the most accurate one.

In the first experiments made with ammonium hydroxide, as will be shown later in the data, the specific conductance had always decreased about 1.9 per cent at 18°, after the heating to 218°. The first three experiments were made without exhausting the air from the bomb; in the third, the bomb was twice reheated, causing further diminutions of 0.6 per cent and 0.25 per cent. In the fourth experiment the air was exhausted down to 4 cm. pressure, which reduced the decrease after the heating to 1.3 per cent. In all cases there was a slight suction when the bomb was opened.

These facts show that some change occurred at the higher temperature which caused a permanent decrease in the conductance. Any contamination would be almost certain to increase it. There was no leak, for the conductance at the upper electrode remained perfectly constant. There was no escape of ammonia through the platinum, for the effect did not continue to an appreciable extent after the second heating. Adsorption by the platinum is not likely, for the effect was almost exactly the same in each run. The most probable explanation is that the oxygen left in the vapor space, in solution, and on the platinum surface, oxidized part of the ammonia to nitrogen and water; this would account also for the decrease of pressure within the bomb, as is evident from the following equation: $4NH_4OH + 3\,O_2 = 2N_2 + 10\ H_2O$; which shows a decrease of one mol of gaseous substances.

The oxidation of ammonia in the presence of platinum black seems to be a well established phenomenon. Henry* observed that platinum sponge caused slow oxidation in a mixture of ammonia and oxygen at 193°. Mond, Ramsey, and Shields† removed oxygen from spongy platinum by this reaction. Vondrácek‡ found that an 0.087 normal solution is oxidized by platinum sponge at ordinary temperatures; boiling solutions of ammonium salts are also oxidized by it. Platinum containing no oxygen had a slight reducing action.

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*Ann. Philos., **25**, 424 (1825).
†Z. phys. Chem., **25**, 657 (1897).
‡Z. anorg. Chem., **39**, 24 (1904).

This difficulty can be partly removed, of course, by pumping the air out as completely as possible. This causes no appreciable loss of ammonia, since its partial pressure above a 0.1 normal solution at 18° is only 1.34 mm;* hence the ammonia present in 20 c.cm. of the vapor above the solution is only 0.01 per cent of that in the solution. But some oxygen still remains dissolved in the solution and in the platinum, and causes oxidation of the ammonia. Hence the most feasible plan was to pump out the air before the heating till the pressure became 2 or 3 cm., and to determine after the heating the strength of the solution, by titrating the solution left in the bomb.

There is some error in the titration of an ammonia solution so dilute as 0.01 normal, as the end point is not sufficiently sharp. The method used was to adopt a standard color, add an excess of acid to a portion of the solution, and titrate to the standard color with the residue of the solution. The percentage error of the titration was at the same time determined by titrating similarly a portion of the unheated solution, whose concentration was known. Solutions 6.1 and 6.2 were titrated with phenacetolin, the correction for the titration-error being + 1.0 per cent; the other dilute solutions were titrated with Congo red, for which correction was — 0.3 per cent.

In the first experiments with ammonium acetate, the conductance at 18° was also found to have decreased from one to two per cent as a result of the heating at 218°. Experiments with acetic acid showed that this was not alone due to the oxidation of ammonia, but that the acetic acid itself had decreased both in conductance and concentration after being heated to 218°. This effect was not sufficiently marked to be taken account of in the work of Noyes and Cooper, probably because in their small temperature-bath the solution could be heated to constant temperature much more quickly, and also because they used unplatinized electrodes, platinum black being a catalyzer of the decomposition, according to the work of Sabatier and Senderens.† In the heatings to 306° this effect was found to become greater with increased concentration of the ammonium acetate solution. It seemed possible that it might be due to the formation of acetamide at the high temperature and the continued existence of this in the solution at 18° owing to the rapid cooling. If this were the case, it should be possible to reconvert it to ammonium acetate by prolonged heating at about 100°. Two hours heating of one of the solutions at 110° - 120°, however, produced only a slight decrease, instead of an increase, in the conductance at 18°. The existence of acetamide in the solutions at the high temperatures would give rise to an error in the calculated hydrolysis. That it does

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*Locke and Forsell, Am. Chem. J., **31, 268 (1904).**

†Ann. chim. phys. **(8), 4, 319, 433.**

not exist in significant quantity even at 306° is shown, however, by the agreement of the ionization-constants for water derived from the experiments with salt solutions of very different concentrations, since in these the percentage of acetamide should vary greatly, owing to its being proportional to the product of the ammonium and acetate ion concentrations.

It was found very difficult to analyze accurately the ammonium acetate solutions left in the bomb. The ammonium content could be determined within 0.2 per cent by making the solution alkaline with sodium hydroxide and distilling off the ammonia into standard sulphuric acid; but even this accuracy could not be obtained in determining the acetic acid. The procedure was therefore changed so as to make the oxidation as small as possible. After the initial 18° measurement, the bomb was set in water at 60°, and was kept evacuated for two or three minutes down to a pressure of a few centimeters; this caused the solution to boil vigorously, so that nearly all the air was carried out of the bomb. Several determinations of the conductance at 18° after this treatment, showed an increase of only 0.2 to 0.3 per cent caused by evaporation of water. It is probably safe to assume that in the pure ammonium acetate solutions there was no appreciable loss of ammonia from the salt, because the hydrolysis is less than 3 per cent and the vapor pressure of ammonia therefore practically inappreciable, and also because the observed change in conductivity was so small. In the solutions containing an excess of ammonium hydroxide or acetic acid the loss of these substances that probably occurred by vaporization is not important, since the concentration of the excess of acid or base needs to be known only approximately. The oxidation at 218° was thus reduced to 0.5 per cent or less. This change in concentration can be corrected for accurately enough by assuming that the change of concentration of ammonium acetate is proportional to the change of specific conductance at 18°. In all the experiments at 306° the same procedure was followed, but the loss by oxidation of the salt could not be kept so low. It was necessary, also, to determine the excess of ammonium hydroxide or acetic acid after each experiment, since the addition of one equivalent of base or acid at 306° produces a much greater change in the hydrolysis and conductance than at 218°. The only practicable method found was to empty and dry the bomb, replace in it a weighed quantity of the solution, weigh in enough acetic acid (or ammonium hydroxide) solution to slightly exceed the free ammonium hydroxide (or acid) present, and determine the conductance of this mixture. Since a small excess of acid or base has no appreciable conductance, the total concentration of the ammonium acetate could be calculated from this conductance; and by subtracting from this the concentration of salt at the end of the experiment, as given by the final conductance at 18°, there was obtained the concentration of free ammonium hydroxide (or free acetic acid) in the solution investigated. It was, however, found that, with solutions containing an excess of *acid,* this excess underwent no considerable change during the heating. That the method is accurate within 0.1 per cent was shown by an analysis of a known ammonium acetate solution containing a known excess of ammonium hydroxide.

This procedure of boiling the solution to remove all air was not used with pure ammonium hydroxide, acetic acid or sodium acetate, because there was no especial advantage in it, since it was in any case necessary to titrate the solution after the heating. The procedure was used, however, in the experiments with ammonium chloride; the correction on the concentration for the vaporization of water was found to be the same as in the ammonium acetate solutions, viz., about 0.3 per cent. In the experiments with ammonium chloride at 306° the concentration of the excess of ammonium hydroxide after the experiment was determined by titration against hydrochloric acid.

The measured conductance of the solution includes that of the water and of the small amount of impurities left in the water. The initial 18° values were corrected by subtracting the conductance, measured in a small Arrhenius cell, of the particular sample of water used in making the solution; for the most probable effect of the impurities is to increase rather than to decrease the conductance of weak acids and bases. As a basis for the correction at the higher temperatures the specific conductance of the water and its impurities was determined by making several heatings with pure water, following exactly the same procedure as in the regular experiments. Both my results (reported in this section) and those obtained in the other investigations of this series show that the conductance at the higher temperatures does not vary much in successive runs, and that it is not proportional to the conductance at 18°.

At 18° the measured conductance of the water is due almost entirely to the impurities, that due to the hydrogen and hydroxide ions being inappreciable; but at 218° and 306° the latter forms a considerable part of the whole. Its amount was determined from a preliminary value of the ionization-constant (K_W) of water, by the formula $\underline{L} = 10^{-3} C_H (\Lambda_H + \Lambda_{OH})$ where C_H (equal to $\sqrt{K_W}$) is the concentration, in equivalents per liter, of the hydrogen (or hydroxide) ions in pure water, and $(\Lambda_H + \Lambda_{OH})$ is the sum of the equivalent conductances of hydrogen and hydroxide ions, calculated by adding the Λ_0 value for sodium hydroxide to the difference between the Λ_0 values for hydrochloric acid and sodium chloride.

Table 71 gives the conductance of the water as actually measured in the bomb and its specific conductance at the temperatures 18°, 218°, and 306°.

TABLE 71.—*Conductance of water.*

Date.	Conductance $\times 10^6$.			Specific conductance $\times 10^6$.		
	18°		218°	18°		218°
	Initial.	Final.		Initial.	Final.	
1905						
Nov. 13...	5.5	7.1	43.8	0.85	1.05	6.55
Nov. 14...	4.4	7.1	35.4	0.65	1.05	5.3
Nov. 14...	3.2	9.4	36.2	0.45	1.4	5.4
Nov. 15...	5.3	9.8	41.1	0.8	1.5	6.15
Mean ...	......	......	......	0.7	1.25	5.85
1906			306°.			306°.
June 4...	6.7	26.9	46.1	1.0	3.9	6.8
June 5...	6.2	7.6	35.7	0.9	1.1	5.2
June 19...	7.9	17.5	70.0	1.2	2.7	10.7
June 20...	6.3	61.5	78.7	0.9	9.4	*12.0
June 28...	8.0	25.5	68.3	1.0	3.9	10.4
Mean ...	......	......	......	1.0	3.6	8.7

*This experiment was given a weight of one-half, because of the abnormally high final conductance at 18°.

The data and results of the calculation of the conductance due to hydrogen-ion and hydroxide-ion are as follows:

Temperature	218°	306°
$\Lambda_H + \Lambda_{OH}$	1565	1654
Specific conductance $\times 10^6$ of conductivity water......	5.85	8.7
" " $\times 10^6$ of H and OH ions.........	3.35	2.1
" " $\times 10^6$ of impurities	2.5	6.6

The observed conductance of the solutions was in every case corrected by subtracting the conductance of the impurities. The fraction which this conductance forms of the conductance of the 10 milli-normal ammonium chloride or sodium acetate solutions is about 0.1 per cent at 18°, 0.03 per cent at 218°, and 0.05 per cent at 306°; and of that of the 100 milli-normal ammonium hydroxide or acetic acid is about 0.2 per cent at 18°, 0.6 per cent at 218°, and 4.0 per cent at 306°.

The correction for the conductance of ionized water at 218° and 306° still remains to be considered. In the solution of pure ammonium hydroxide and acetic acid this correction is negligible, even in the most dilute solutions, since the ionization of the base or acid is still sufficient to drive that of the water back to an inappreciable quantity. In the solutions of pure ammonium acetate, where very nearly equal quantities of acid and base are produced by the hydrolysis, the conductance of the hydrogen and hydroxide ions as given in the preceding table was directly subtracted. In the case of the ammonium chloride and the sodium acetate solutions at 218° or 306° this correction is conveniently calculated in combination with the correction for the hydrolysis of the salt, which is not entirely negligible even in the presence of the excess of ammonium hydroxide or acetic acid added. And in the case of the ammonium acetate solutions containing an excess of ammonium hydroxide or acetic acid at 218° and 306°, the water correction is best combined with that for the conductance of the excess of base or acid present. Thus in the solutions of ammonium chloride or acetate containing an excess of the hydroxide, the concentration of un-ionized ammonium hydroxide is approximately equal to the concentration of the ammonium hydroxide added (C_B) plus that (Ch) arising from the hydrolysis of the salt (the latter term Ch being negligible in the case of the chloride); and that of the ammonium-ion is given approximately by the ratio (multiplied by 10^3) of the specific conductance of the solution ($\underline{L}$), to the equivalent conductance Λ_0 of the completely ionized salt. The combination of the expressions of these two facts with the mass-action equations for ammonium hydroxide and water gives the formulas:

$$C_{OH} = 10^{-3}\frac{K_B\Lambda_0(C_B + Ch)}{\underline{L}} \quad \text{and} \quad C_H = \frac{K_W}{C_{OH}}$$

where the concentrations (both those given directly and those involved in K_B and K_W) are expressed in equivalents per liter. In the ammonium chloride solutions part of the hydrogen corresponds to the excess of chloride-ion over ammonium-ion, the remainder to the hydroxide-ion in the solution; hence the correction to be subtracted from the specific conductance is:

$$10^{-3}[C_{OH}\ (\Lambda_H + \Lambda_{OH}) + (C_H - C_{OH})\ (\Lambda_H + \Lambda_{Cl})]$$

In the ammonium acetate solutions, on the other hand, part of the hydroxide-ion corresponds to the excess of ammonium-ion over acetate-ion, and the remainder to the hydrogen-ion in the solution; hence the correction to be subtracted is:

$$10^{-3}\ [C_H\ (\Lambda_H + \Lambda_{OH}) + (C_{OH} - C_H)\ (\Lambda_{NH_4} + \Lambda_{OH})]$$

The calculations are in every way similar for sodium acetate and for ammonium acetate with excess of acetic acid, K_A and C_A being substituted for K_B and C_B, and C_H for C_{OH}; the correction to the specific conductance then becoming

$$10^{-3}\ [C_H(\Lambda_H + \Lambda_{OH}) + (C_{OH} - C_H)\ (\Lambda_{Na} + \Lambda_{OH})]$$

for sodium acetate, and

$$10^{-3}\ [C_{OH}(\Lambda_H + \Lambda_{OH}) + (C_H - C_{OH})\ (\Lambda_H + \Lambda_{Ac})\ ]$$

for ammonium acetate.

At 18°, in the solutions of ammonium chloride and sodium acetate, the ionization of water is so small that the above mentioned hydrolysis correction entirely disappears; on the contrary, the conductance of the added base or acid itself must be subtracted. This correction is calculated by the mass-action law to be

$$10^{-6}K_BC_B\frac{(\Lambda_{NH_4}+\Lambda_{Cl})}{\underline{L}}(\Lambda_{NH_4}+\Lambda_{OH})$$

for the ammonium hydroxide in the ammonium chloride solution, and $10^{-6}K_AC_A\frac{\Lambda_{Na}+\Lambda_{Ac}}{\underline{L}}(\Lambda_H+\Lambda_{Ac})$ for the acetic acid in the sodium acetate solution; where K_B (or K_A) is the ionization constant of the base (or acid), C_B (or C_A) is the concentration of the added base (or acid) in equivalents per liter, Λ_{NH_4}, Λ_{Cl} and Λ_{OH} (or Λ_{Na}, Λ_{Ac} and Λ_H) are the equivalent conductances of the respective ions, and $\underline{L}$ is the specific conductance of the salt in the mixture.

The effect of the excess of acid or base upon the ionization of the salt remains to be considered. In almost all cases this is negligible, as is apparent from the smallness of the correction for its conductance; but in the dilute solutions of ammonium chloride and sodium acetate at 18°, the concentration of the common ion from the added base or acid is sufficient to diminish appreciably the ionization of the salt itself, so that the conductance obtained by subtracting that of the base or acid is not the true conductance of the salt at the concentration in question. However, no correction was applied for this, since these 18° measurements were made only to show whether any contamination or change had taken place in the solution during the heating.

The concentration is diminished in the case of the more volatile solutes by the volatilization of a small amount of the solute. In the case of acetic acid at 218°, Noyes and Cooper (section 49, Part V) have already shown that the concentration is not appreciably affected by vaporization into the small vapor-space of 2 or 3 c.cm. usually present. The total correction to be applied to the concentration for the vaporization of both water and solute was directly determined for ammonia at 218° and 302° and for acetic acid at 306° by measuring the difference in conductance produced by increasing the vapor-space from 2 c.cm. to 30 or 50 c.cm. Without describing the details of the experiments or of the calculation, the results may be stated. It was found that the correction to be made on the concentration per cubic centimeter of vapor-space in the case of ammonium hydroxide solutions is —0.025 per cent at 218° and —0.12 per cent at 302° or 306°, and in the case of the acetic acid solutions is —0.05 per cent at 306°. Thus the correction is negligible at 218° for the ammonium hydroxide just as for acetic acid, and is small for both substances even at 306°.

80. THE SPECIFIC-VOLUME DATA.

To change the concentration by weight to concentration by volume at the temperature (*t*) of the measurement, the number of milli-equivalents per kilogram of solution was multiplied by the density of the solution at 4° and by the ratio of the specific volume at 4° to that at *t*°. The density was taken as unity in most cases, but special values were used in the case of solutions stronger than 0.04 normal.*

Noyes and Coolidge† have found that sodium and potassium chlorides in 0.1 normal solution have substantially the same specific-volume ratio at 306°, and that this specific-volume ratio differs from that of water by only 1.0 per cent. Since the solutions of ammonium chloride, sodium acetate, and ammonium acetate used in the present work were all less than 0.03 normal at 306°, it was considered unnecessary to determine the specific-volume ratios for them; but these were assumed to be the same as for sodium and potassium chlorides, and the deviation from the ratio for pure water was assumed proportional to the concentration. At 18°, in all cases, the specific-volume ratio for pure water, 1.0013, was used.

For ammonium hydroxide and acetic acid, determinations of the specific-volume ratio were made at the highest temperature on solutions sufficiently strong to show the deviation from pure water. For corrections at smaller concentrations, and at 218°, the deviation from the ratio for pure water was assumed proportional to the concentration and to the temperature difference. The error introduced by this assumption can not be greater than 0.1 per cent.

The procedure for determining specific volume was the same as that employed by Noyes and Coolidge. In table 72 the first column gives the date; the second, the concentration in milli-equivalents per kilogram of solution; the third, the weight (in vacuo) of the solution in grams; the fourth, the temperature of measurement (*t*°); the fifth, the volume of the solution at this temperature; the sixth, the weight of solution corrected for vaporization into the vapor-space; the seventh, the specific volume of the solution at *t*°; the eighth, the specific volume corrected to 302° (or 306°) by adding 0.0043 per degree; and the ninth, the ratio of the specific volume at *t*° to that at 4°.

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*The values of the density employed are as follows:

Ammonia 0.1	normal	0.9992	Determined by pycnometer.
Ammonia 0.5	normal	0.9961	Lunge *et al.*, Landolt-Börnstein-Meyerhoffer's Tabellen, 329 (1905).
Acetic acid 0.1	normal	1.0011	
Acetic acid 0.5	normal	1.0042	Reyher, *ibid.*, p. 344.
Ammonium chloride 0.04	normal	1.0007	Dijken, *ibid.*, p. 336.
Sodium acetate 0.04	normal	1.0020	Franz, *ibid.*, p. 335.
Ammonium acetate 0.04	normal	1.0008	Hager, *ibid.*, p. 320.

†Section 12, Part II.

The specific-volume ratio for water at 302° is 1.417; at 306° 1.4365. The values for the ammonium hydroxide and acetic acid solutions therefore differ from that for water by 1.5 per cent and by 0.6 per cent respectively.

The two determinations of the volume of the bomb, made for the above measurements, gave 127.9 c.cm. and 128.0 c.cm. respectively for the volume at zero, which corresponds to 129.5 c.cm. at 306°. The values of the thermal expansion-coefficient of the bomb, by means of which the latter value was calculated, are reported in section 21, Part III.

TABLE 72.—*The specific-volume data.*

AMMONIUM HYDROXIDE.

Date.	Milli-equivalents per kilogram.	Weight of solution.	Temperature (t°).	Volume at t°.	Weight at t°.	Specific volume		
						At t°.	At 302°.	Ratio 302°/4°.
1906								
Feb. 27 ..	523	88.69	300.8	127.48	88.61	1.4387	1.444	1.438
Mar. 3 ..	513	88.56	301.5	127.61	88.49	1.4421	1.4445	1.4385
Mean ..	......	......	......	......	......	......	......	1.4385

ACETIC ACID.

Date.	Milli-equivalents per kilogram.	Weight of solution.	Temperature (t°).	Volume at t°.	Weight at t°.	Specific volume		
						At t°.	At 306°.	306°/4°
1906								
May 13 ..	431	88.13	305.1	126.54	88.02	1.4376	1.4415	1.447
May 15 ..	431	88.60	306.0	127.36	88.53	1.4386	1.4385	1.444
Mean ..	......	......	......	......	......	......	......	1.4455

81. CONDUCTANCE-CAPACITY OF THE APPARATUS.

The conductance-capacity was determined by measuring the conductance in the bomb of solutions of known strength, and dividing these values into the known specific conductance of the solutions as determined by Kohlrausch.* These solutions were made to contain at 18° an exact number of equivalents in one liter. In table 73, the fifth column gives the measured conductance of the solution; all the measurements in 1905 having been made at 17.95°, those in 1906, at 18.00°. The sixth column gives the conductance reduced to 18.00° and corrected for the conductance of the water. The seventh and eighth give the conductance-capacities at 18°, and at 218° or 306° respectively.

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*Sitzungsber. königl. preuss. Akad., 1900, 1002. The values used were:

Potassium chloride,	0.01 normal,	122.43
	0.005	124.41
Potassium nitrate,	0.01	118.19
	0.005	120.47
Sodium chloride,	0.01	101.95
	0.02	99.62

TABLE 73.—*Values of the conductance-capacity.*

Conductance vessel.	Date.	Salt.	Milli-equivalents per liter.	Conductance × 10^6.		Conductance-capacity.	
				Observed.	Corrected.	18°	218°
	1905						
Bomb 4	Apr. 6 ..	KCl....	10.00	8,171	8,172	0.14983	......
		KCl....	10.00	8,175	8,176	0.14974	......
		KCl....	10.00	8,173	8,174	0.14977	......
	Apr. 7 ..	KCl....	10.00	8,171	8,172	0.14983	......
	Apr. 8 ..	KNO_3..	10.00	7,888	7,889	0.14982	......
		Mean ..	....	......	......	0.14980	0.14941
Bomb 4	July 22 ..	KCl....	10.00	8,154	8,157	0.15010	......
	July 23 ..	KCl....	5.00	4,147.5	4,146.5	0.15002	......
	July 24 ..	KNO_3..	5.00	4,023.5	4,019.5	0.14985	......
		NaCl...	10.00	6,802	6,801.5	0.14989	......
		Mean ..	....	......	......	0.14997	0.14958
	1906						306°
Bomb 4	Feb. 12 ..	KCl....	10.00	8,228	8,220	0.14894	......
		NaCl...	10.00	6,855	6,847	0.14890	......
		Mean ..	....	......	......	0.14892	0.14828
Bomb 4	*Feb. 12 .	KCl....	10.00	8,191	8,183	0.14962	......
		NaCl...	10.00	6,824.5	6,816.5	0.14956	......
		Mean ..	....	......	......	*0.14959	......
Bomb 4	Mar. 2 ..	NaCl...	10.00	6,950	6,942	0.14686	......
	Mar. 11 ..	KCl....	10.00	8,351	8,344	0.14673	......
		Mean ..	....	......	......	0.14680	0.14617
Bomb 4	Apr. 23 ..	KCl....	10.00	8,342	8,334	0.14691	......
	May 16 ..	KCl....	10.00	8,342	8,334	0.14691	......
	June 6 ..	KCl....	10.00	8,355	8,346	0.14669	......
		Mean ..	....	......	......	0.14687	0.14624
Bomb 3	June 22 ..	KCl....	10.00	7,990	7,981	0.15340	......
		KCl....	10.00	7,987	7,980	0.15343	......
		Mean ..	....	......	......	0.15341	0.15275
Bomb 3	June 25 ..	KCl....	10.00	8,010	8,002	0.15300	0.15234
Bomb 3	June 29 ..	KCl....	10.00	8,021	8,013	0.15280	......
	July 2 ..	KCl....	10.00	8,015	8,008	0.15280	......
		Mean ..	....	......	......	0.15284	0.15218
Bomb 3	July 3 ..	KCl....	10.00	912.5	911.6	1.3431	1.3346
	1905						
Pipette-Cell	July 12 ..	KCl....	10.01	2,619.5	2,620.4	0.4679	......
		KCl....	10.01	2,621.5	2,622.4	0.4674	......
		NaCl...	9.99	2,176.8	2,177.1	0.4678	......
	July 13 ..	NaCl...	20.00	4,258.3	4,259.9	0.4677	......
		KNO_3..	10.00	2,527.0	2,527.6	0.4676	......
		Mean ..	....	......	......	0.4677	......

*In this case the bomb contained only 60 c.cm. of solution.

The comparison of the first two mean values in table 73 shows an increase in the conductance-capacity of only 0.1 per cent in four months; and the close agreement in the specific conductance of the same ammonium chloride solution, measured in the bomb and in the pipette cell at the close of the measurements at 218° (see table 74, experiments 1.5 a and 1.5 b) shows that the conductance-capacity had remained practically constant up to that time. But when redetermined after the first five experiments at 302° (see table 76, experiments 10 a – 10 e) the conductance-capacity had decreased by 0.65 per cent. A comparison of the initial data at 18° of these five experiments showed that three-fourths of this change took place at the first heating to 302°, which was made for the purpose of steaming out the bomb. The remaining 0.2 per cent change was therefore distributed equally over the five experiments.

Just before March 2, 1906, the lower electrode was removed, replaced, and replatinized, the conductance-capacity being thereby changed. The succeeding determinations show that it remained constant at the new value. The last two determinations of February 12, 1906, in table 73, were made with only 60 c.cm. of solution in the bomb. The conductance-capacity was increased 0.45 per cent by this change in the depth of the solution; it was found independent of the depth when the volume of the solution exceeded 85 c.cm. (See section 78).

The electrode of bomb No. 3 was replatinized after the experiment of June 20, 1906, and was removed, replaced, and replatinized before the experiment of June 28, the conductance-capacity being changed slightly each time. On July 3, the cylindrical electrode was removed, and a quartz cup put in, for work with the stronger ammonium chloride and sodium acetate solutions.

82. THE CONDUCTIVITY DATA.

In the following tables are recorded the data actually observed,* which form the basis of subsequent theoretical calculations. For convenience there are also included in these tables the corrections for impurities in the water, and for the residual hydrolysis or for the added base or acid in the case of ammonium chloride and sodium acetate, which corrections were discussed in section 78.

The first column gives the date of the experiment. The second gives the number of the experiment; the figure before the decimal point is the number of the stock solution, that after the decimal point the number of the dilute solution prepared from the stronger one; successive runs with the same solution are designated by appending the letters a, b, etc. In the next column or columns is given the concentration of the solute or solutes in milli-equivalents (referred to the oxygen-equivalent as 8.000) per kilogram of solution. The column headed temperature (*t*) gives the temperature of the measurement in degrees centigrade on the hydrogen scale. The next column gives the measured conductance in reciprocal ohms, multiplied by 10^6 and corrected for calibration and lead resistance. (The letter G shows that the data were obtained in the glass cell of pipette form.)

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*Ten experiments at 218°, and fifteen at 306°, were rejected on account of leakage of solution out of the bomb. The initial 18° measurements on these solutions were usually not affected, and have therefore been included among the data. Three other experiments at 218°, and one other at 306°, were not used in deriving final values on account of an abormal difference between the initial and final conductances at 18°; but the data of these experiments are given for the sake of completeness. In addition, several measurements with ammonium acetate at 218° have been omitted, because a more complete and accurate series was made later.

In tables 74 and 75, the next four columns give the values of the specific conductance multiplied by 10^6. The first of the four gives the uncorrected value, obtained by multiplying the measured conductance by 10^6 and by the conductance-capacity given in table 73 for the date next preceding that of the experiment; the second gives the values obtained from these by subtracting the conductance of the impurities of the water given in section 79; and the third and fourth give the same values further corrected as described in section 79 for the conductance of the added base (or acid) at 18° and for the ionized water and residual hydrolysis at the higher temperatures. The last column gives the equivalent conductance, calculated by dividing the corrected specific conductance by the number of equivalents per liter at $t°$. These last were derived from the milli-equivalents per kilogram as described in section 80, and are given in tables 80 and 81.

In tables 76 and 77 the sixth and seventh columns contain the specific conductances, uncorrected, and corrected for the conductance of the impurities in the water. The last two columns contain the corresponding equivalent conductances. Both are given since there may be some question in these cases as to the way in which the water correction should be applied.

In table 78, which contains the results with ammonium acetate, the equivalent conductances are not given, since the subsequent calculations are based on the specific conductances. The last column of the table gives the percentage change of the specific conductance at 18°, due to oxidation or decomposition. The values of milli-equivalents of salt per kilogram corresponding to the conductance at the higher temperature and to the final conductance at 18° were obtained from the initial content by changing it by a percentage amount equal to the above mentioned percentage change in conductance. No similar correction was applied to the acid or base content, except in the case of the experiments carried to 306° with solutions containing an excess of base, in which case the change in content was directly determined, as described in section 79, to be that given in the table.

TABLE 74.—*Conductivity data on ammonium chloride.*

Date.	Experiment No.	Milli-equivalents per kilogram.		Temperature $t°$.	Conductance $\times 10^6$.	Specific conductance $\times 10^6$.				Equivalent conductance.
		NH_4Cl.	NH_4OH.			Uncorrected.	Corrected for			
							Impurities.	NH_4OH.	Water and HCl.	
1905										
Nov. 17	1.1	10.90	......	17.98	2,845 G	1,330.5	1,329.5	......	......	122.15
		10.90	......	25.00	3,288 G	1,538	1,537	......	......	141.35
Nov. 19	1.2a	2.359	1.21	17.98	2,009	301.4	300.8	298.6	......	126.8
Nov. 20	1.2b	2.359	1.21	17.98	2,010	301.5	300.9	298.7	......	126.85
		2.366	1.21	218.1	10,760	1,610	1,607.5	......	1,601	802.6
		2.366	1.21	17.98	2,041	306.1	304.8	302.6	......	128.1
Nov. 21	1.3a	2.241	1.21	17.98	1,911	286.6	285.9	283.7	......	126.75
		2.248	1.21	218.6	10,240	1,531.5	1,529	......	1,522.5	804.0
		2.248	1.21	17.98	1,922	288.2	286.9	284.7	......	126.85
Nov. 22	1.3b	2.241	1.21	17.98	1,917	287.5	286.8	284.6	......	127.2
		2.248	1.21	218.3	10,255	1,534	1,531.5	......	1,525	805.0
		2.248	1.21	17.98	1,929	289.2	287.9	285.7	......	127.3
Nov. 22	1.4	10.03	5.95	17.98	8,224	1,233.5	1,232.5	1,230	......	122.8
		10.06	5.95	218.2	43,470	6,503	6,500	......	6,494	765.9
		10.06	5.95	17.98	8,263	1,239	1,238	1,235.5	......	123.0
Nov. 23	2	12.08	5.90	17.98	9,838	1,475.5	1,474.5	1,472.5	......	122.1
		12.115	5.90	217.8	51,785	7,746	7,744	......	7,738	757.1
		12.115	5.90	17.98	9,877	1,481.5	1,480	1,478	......	122.15
Dec. 19	1.5a	12.065	......	18.00	3,142 G	1,469	1,468	......	......	121.85
Dec. 20	1.5b	12.065	......	18.00	9,799	1,469.5	1,468.5	......	......	121.9
Dec. 22	1.6	2.255	......	18.00	610 G	285.3	284.4	......	......	126.3
				25.00	705 G	329.9	328.9	......	......	146.25
1906										
May 28	1.7	2.901	8.64	18.00	2,600	381.5	380.9	368.4	......	127.15
		2.905	7.30	304.6	14,515	2,120.5	2,115	......	2,092	1,028
		2.905	7.30	18.00	2,624	384.9	381.3	370.8	......	127.8
May 29	1.8	2.855	15.18	18.00	2,632	386.0	385.4	363.1	......	127.35
		2.856	13.13	305.0	14,300	2,088.5	2,083	......	2,075	1,038
		2.856	13.13	18.00	2,658	390.0	386.4	367.3	......	128.8
June 30	1.9	14.295	26.30	18.00	11,420	1,745.5	1,745	1,737	......	121.65
		14.295	25.95	304.4	61,020	9,287	9,282	......	9,253	922.5
		14.295	25.95	18.00	11,450	1,750.5	1,747	1,739	......	121.8
July 5	1.10	43.45	43.83	18.00	3,759	5,048	5,047	5,042	......	116.15
		43.45	43.34	305.5	18,930	25,265	25,260	......	25,215	827.5
		43.45	43.34	18.00	3,764	5,056	5,052	5,047	......	116.3

TABLE 75.—*Conductivity data on sodium acetate.*

Date.	Experiment No.	Milli-equivalents per kilogram.		Temperature $t°$.	Conductance $\times 10^6$.	Specific conductance $\times 10^6$.				Equivalent conductance.
		CH_3CO_2Na	CH_3CO_2H			Uncorrected.	Corrected for			
							Impurities.	$HC_2H_3O_2$	Water and NaOH	
1906										
June 21	1.1	2.848	8.82	18.00	1,530.5	234.8	234.2	214.2	......	75.3
		2.848	7.46	304.5	10,505	1,604.5	1,599	......	1,586	794
		2.848	7.46	18.00	1,534.5	235.4	231.8	214.9	......	75.55
June 22	1.2	2.810	14.46	18.00	1,607.5	246.6	246.0	213.0	......	75.9
		2.810	11.57	304.5	10,355	1,581.5	1,576.5	......	1,569	797
		2.810	11.57	18.00	1,605.5	246.3	242.7	216.3	......	77.1
July 1	1.3	14.15	23.30	18.00	6,671	1,019.5	1,018.5	1,007.5	......	71.3
		14.15	21.99	304.8	45,700	6,955	6,950	......	6,929	698.5
		14.15	21.99	18.00	6,666	1,019	1,015	1,004.5	......	71.1
July 3	1.4	42.49	47.67	18.00	2,123	2,851	2,850	2,842	......	66.85
		42.49	45.29	304.6	13,685	18,265	18,260	......	18,230	608.5
		42.49	45.29	18.00	2,122.5	2,851	2,847	2,840	......	66.8

TABLE 76.—*Conductivity data on ammonium hydroxide.*

Date.	Experiment No.	Milli-equivalents per kilogram.	Temperature $t°$.	Conductance × 10^6	Specific conductance × 10^6.		Equivalent conductance.	
					Un-corrected.	Corrected.	Un-corrected.	Corrected.
1905								
Feb. 21...	1a	99.9	17.95	2,067	310.2	309.7	3.111	3.106
Feb. 25...	1b	99.9	17.95	2,066.5	310.1	309.6	3.110	3.105
Apr. 14...	2a	103.45	17.95	2,104.5	315.3	314.6	3.055	3.048
			216.9	3,047	455.2	452.7	......	......
			17.95	2,065.5	309.5	308.2	......	......
Apr. 15...	2b	103.45	17.95	2,104	315.2	314.5	3.054	3.047
			216.9	3,078	459.9	457.4	......	......
			17.95	2,067.5	309.8	308.5	......	......
Apr. 18...	2c	103.45	17.95	2,105	315.3	314.6	3.055	3.048
			217.1	3,105	464.0	461.5	......	......
			17.95	2,068	309.9	308.6	......	......
			217.1	3,106	464.1	461.6	......	......
			17.95	2,055	307.9	306.6	......	......
			217.6	3,094	462.3	459.8	......	......
			17.95	2,049.5	307.1	305.8	......	......
Apr. 21...	2d	103.45	17.95	2,104.5	315.3	314.6	3.055	3.048
			216.5	3,087	461.3	458.8	......	......
			17.95	2,078	311.4	310.1	......	......
June 8...	3	89.6	17.95	1,964.5	294.3	293.6	3.292	3.284
June 10...	4	94.05	17.95	2,009.5	301.0	300.5	3.208	3.203
		92.9	217.3	2,889	431.6	429.1	5.520	5.488
		92.9	17.95	1,992.5	308.5	297.2	3.220	3.206
June 17...	5a	106.85	17.95	2,140	320.6	320.0	3.008	3.002
		105.8	217.7	3,067	458.3	455.8	5.151	5.122
		105.8	17.95	2,117	317.3	316.0	3.006	2.994
June 19...	5b	106.85	17.95	2,139	320.4	319.8	3.006	3.000
June 20...	*5c	106.85	17.95	2,137	320.1	319.5	3.003	*2.997
		105.35	217.7	3,078	460.0	457.5	5.136	5.108
		105.35	17.95	2,110	316.1	314.8	3.007	2.995
June 21...	*5d	106.85	17.95	2,140	320.6	320.0	3.008	*3.002
		105.6	217.4	3,081	460.3	457.8	5.125	5.097
		105.6	17.95	2,108.5	316.0	314.7	2.998	2.986
June 25...	6	85.95	17.95	1,923	288.0	287.2	3.358	3.349
June 30...	6.1	9.35	17.95	627.4	94.0	93.1	10.06	9.97
		8.965	217.7	952.5	142.3	139.8	18.83	18.49
		8.965	17.95	618.7	92.7	91.4	10.35	10.21
July 4...	6.2	10.17	17.95	652.1	97.7	97.2	9.52	9.57
		9.785	217.5	969.5	144.9	142.4	17.55	17.25
		9.785	17.95	637.9	95.6	94.3	9.78	9.65
July 21...	7a	89.9	17.95	629.9 G	294.6	294.1	3.283	3.278
July 21...	*7b	89.9	17.95	1,963	294.4	293.9	3.280	*3.275
		88.9	217.4	2,846	425.7	423.2	5.617	5.583
		88.9	17.95	1,933.5	290.1	288.8	3.269	3.255
Oct. 17...	8	146.45	17.95	799.6 G	373.9	373.2	2.560	2.555
Nov. 3...	9	134.55	17.95	767.1 G	358.8	358.1	2.673	2.668
		134.55	24.97	893.6 G	418.0	417.2	3.119	3.113
Nov. 4...	9.1a	10.51	17.95	660.6	99.1	98.6	9.45	9.40
Nov. 5...	9.1b	10.51	17.95	662.2	99.3	98.8	9.47	9.42
		9.715	218.0	934	139.7	137.2	17.06	16.76
		9.715	17.95	631.0	94.7	93.4	9.75	9.62
Nov. 7...	9.2	12.705	17.95	730.5	109.6	109.1	8.63	8.59
		12.165	217.2	1,072	160.4	157.9	15.63	15.39
		12.165	17.95	713.6	107.1	105.8	8.82	8.71

*33.5, 33, and 38 c.cm. of vapor space respectively in experiments 5c, 5d, and 7b.

TABLE 76.—*Conductivity data on ammonium hydroxide*—Continued.

Date.	Experiment No.	Milli-equivalents per kilogram.	Temperature t°.	Conductance $\times 10^6$.	Specific conductance $\times 10^6$.		Equivalent conductance.	
					Uncorrected.	Corrected.	Uncorrected.	Corrected.
1905								
Nov. 9...	9.3	12.645	17.95	730.0	109.6	109.0	8.68	8.63
		10.97	217.5	1,032	154.4	151.9	16.69	16.41
		10.97	17.95	692.9	104.0	102.7	9.49	9.37
Nov. 11...	9.4	13.635	17.95	759.5	114.0	113.4	8.38	8.33
		12.36	217.7	1,069.5	160.0	157.5	15.35	15.11
		12.36	17.95	718.4	107.8	106.5	8.74	8.63
1906								
Feb. 3...	10a	147.55	18.00	2,511	375.5	374.9	2.551	2.547
		134.1	301.8	1,054	156.7	150.2	1.671	1.601
		134.1	18.00	2,440	364.6	361.0	2.725	2.698
Feb. 5...	†10b	147.55	18.00	2,513	375.5	374.8	2.551	†2.546
		137.15	301.0	1,041.5	154.9	148.3	1.612	1.544
		137.15	18.00	2,368	353.5	349.9	2.584	2.557
Feb. 6...	‡10c	147.55	18.00	2,501	375.0	374.4	2.548	2.544
		126.35	301.8	985.5	146.3	139.7	1.809	‡1.728
		126.35	18.00	2,315	346.9	343.3	2.752	2.723
Feb. 7...	‡10d	147.55	18.00	2,506	375.5	374.8	2.551	§2.546
		97.2	301.9	858.5	127.4	120.8	2.065	‡1.959
		97.2	18.00	2,094	313.5	309.9	3.232	3.195
Feb. 9...	§10e	147.55	18.00	2,516	375.0	374.4	2.548	2.544
		147.55	25.00	2,927	436.3	435.5	2.969	§2.963
		98.1	301.8	905	134.2	127.6	1.958	1.862
		98.1	25.00	2,411	359.1	355.5	3.673	3.636
Feb. 20...	11	522.8	18.00	4,528	674.3	673.6	1.297	1.295
Mar. 9...	12	512.9	18.00	4,574	671.4	670.6	1.316	1.315
		462.2	301.1	1,922	280.9	274.3	0.879	0.859
		462.2	18.00	4,296	630.6	627.0	1.371	1.363
May 23...	13a	420.9	18.00	4,171	612.8	611.9	1.463	1.461
		416.2	305.7	1,609	235.4	228.8	0.826	0.803
		416.2	18.00	4,100	602.4	598.8	1.454	1.445
May 23...	13b	420.9	18.00	4,174	613.2	612.3	1.464	1.462
		416.8	305.3	1,650	241.4	234.8	0.845	0.822
		416.8	18.00	4,103	602.8	599.2	1.453	1.444
May 25...	13c	420.9	18.00	4,183	614.5	613.6	1.467	1.465
		413.8	305.0	1,670.5	244.3	237.7	0.859	0.836
		413.8	18.00	4,099	602.2	598.6	1.462	1.453
May 26...	13.1a	145.2	18.00	2,525	370.9	370.2	2.561	2.556
		138.8	305.0	972.5	142.3	135.7	1.479	1.411
		138.8	18.00	2,449	359.7	356.1	2.598	2.571
May 27...	13.1b	145.2	18.00	2,518	370.0	369.3	2.554	2.549
		138.0	304.8	974	142.5	135.9	1.488	1.420
		138.0	18.00	2,451	360.1	356.5	2.616	2.590

†Experiment 10b was rejected, since the heating was much shorter than in the other experiments, and its results show considerable deviation from the others.

‡46 and 50 c.cm. of vapor space respectively in experiments 10c and 10d.

§The air was boiled out of the solution after the initial measurements in experiments 10d and 10e.

TABLE 77.—*Conductivity data on acetic acid.*

Date.	Experiment No.	Milli-equivalents per kilogram.	Temperature t°.	Conductance $\times 10^6$.	Specific conductance $\times 10^6$.		Equivalent conductance.	
					Un-corrected.	Corrected.	Un-corrected.	Corrected.
1905								
July 14...	1	91.35	17.95	961 G	449.5	448.9	4.924	4.917
July 17...	2	109.1	17.95	1,046 G	489.2	488.6	4.487	4.481
July 18...	3a	97.5	17.95	989.5 G	462.9	462.2	4.751	4.744
Aug. 11...	3b	97.5	17.95	3,080.5	462.0	461.3	4.741	4.734
		97.0	217.8	2,935.5	439.1	436.6	5.370	5.340
		97.0	17.95	3,059	458.7	457.5	4.731	4.719
Aug. 13...	3c	97.5	17.95	3,077	461.4	460.7	4.735	4.728
		96.95	217.5	2,946	440.7	438.2	5.391	5.361
		96.95	17.95	3,065	459.7	458.4	4.744	4.730
Oct. 10...	4	209.9	17.95	1,453 G	679.4	678.6	3.235	3.231
*May 5...	5.1a	143.5	18.00	3,837	563.6	562.7	3.928	3.921
		144.45	304.6	1,178.5	172.4	165.8	1.712	1.646
		144.45	18.00	3,793	557.3	553.7	3.858	3.833
*May 7...	5.1b	143.5	18.00	3,835	563.4	562.5	3.926	3.920
		144.15	305.1	1,148	167.95	161.3	1.673	1.607
		144.15	18.00	3,788	556.5	552.9	3.869	3.844
May 8...	5.1c	143.5	18.00	3,833	563.1	562.2	3.924	3.918
		142.7	305.3	1,122.5	164.2	157.6	1.651	1.585
		142.7	18.00	3,782	555.6	552.0	3.894	3.868
May 13...	6a	432.5	18.00	6,490	953.5	953	2.200	2.198
		431.3	305.1	1,792	262.1	255.5	0.873	0.851
		431.3	18.00	6,363	935	931.5	2.163	2.154
May 15...	6b	432.5	18.00	6,489	953.5	953	2.199	2.198
		431.2	306.0	1,768	258.6	252.0	0.864	0.842
		431.2	18.00	6,368	935.5	932	2.165	2.156
May 18...	†6c	432.5	18.00	6,464	954	953.5	2.201	2.200
		431.3	304.9	1,787.5	261.5	254.9	0.893	0.871
		431.3	18.00	6,353	937.5	934	2.169	2.160
May 20...	†6d	432.5	18.00	6,458	953	952.5	2.199	2.197
		430.8	305.1	1,783.5	260.9	254.3	0.895	0.872
		430.8	18.00	6,342	936	932.5	2.168	2.159

*In experiments 5.1a and 5.1b the solution was boiled for a few minutes after the measurement at 18°.

†39 and 42 c.cm. of vapor space in experiments 6c and 6d respectively.

TABLE 78.—*Conductivity data on ammonium acetate.*

Date.	Experiment No.	Milli-equivalents per kilogram.			Temperature t°.	Conductance × 10⁶.	Specific conductance × 10⁶.		Percentage change at 18°.
		$NH_4C_2H_3O_2$	NH_4OH	$HC_2H_3O_2$			Uncorrected.	Corrected for impurities.	
1905									
July 29..	1.3	14.595	......	......	17.95	8,738	1,310.5	1,310	......
Aug. 2..	1.4	14.46	......	......	17.95	8,678	1,301.5	1,300.5	......
Oct. 18..	2.1	14.03	......	......	17.95	8,439	1,265.5	1,264.5	......
					217.8	25,280	3,781	3,779	......
					17.95	8,420	1,262.5	1,261	—0.3
Oct. 19..	2.2	7.11	......	......	17.95	4,373	655.7	655.1	......
					217.9	12,875	1,925.5	1,923	......
					17.95	4,328	649.1	647.8	—1.1
Oct. 21..	*2.3a	7.18	7.19	......	17.95	4,462	669.2	668.5	......
					217.5	17,270	2,583	2,580	......
					17.95	4,529	679.2	677.9	+1.4
Oct. 22..	*2.3b	7.18	7.19	......	17.95	4,461	669.0	668.3	......
					217.6	16,905	2,529	2,526	......
					17.95	4,585	687.6	686.3	+2.7
Oct. 23..	2.4a	7.15	7.41	......	17.95	4,464	669.4	668.6	......
					217.8	17,210	2,574	2,572	......
					17.95	4,446	666.7	665.4	—0.5
Oct. 24..	2.4b	7.15	7.41	......	17.95	4,470	670.3	669.5	......
					217.8	17,205	2,574	2,571	......
					17.95	4,477	671.3	670.0	+0.1
Oct. 26..	2.5a	7.15	13.97	......	17.95	4,473	670.8	670.3	......
					218.0	19,285	2,885	2,882	......
					17.95	4,476	671.2	669.9	—0.05
Oct. 27..	2.5b	7.15	13.97	......	17.95	4,477	671.4	670.9	......
					217.9	19,215	2,874	2,872	......
					17.95	4,473	670.7	669.4	—0.2
Oct. 28..	2.6	7.13	28.02	......	17.95	4,532	679.6	679.0	......
					218.1	21,130	3,161	3,158	......
					17.95	4,541	681.1	679.8	+0.1
Oct. 30..	2.7	14.24	14.32	......	17.95	8,625	1,293.5	1,292.5	......
					218.2	33,495	5,010	5,007	......
					17.95	8,635	1,295	1,293.5	+0.1
Oct. 31..	2.8	14.125	27.75	......	17.95	8,593	1,288.5	1,287.5	......
					217.8	36,775	5,501	5,498	......
					17.95	8,599	1,289.5	1,288	+0.05
Nov. 1..	2.9	14.155	55.43	......	17.95	8,679	1,301.5	1,300.5	......
					217.9	40,865	6,113	6,110	......
					17.95	8,642	1,296	1,294.5	—0.5
Nov. 24..	2.10	7.12	......	......	17.98	4,383	657.3	656.7	......
					217.5	13,095	1,958.5	1,956	......
					17.98	4,401	660.0	658.7	+0.3
Nov. 25..	2.11	7.055	......	......	17.98	4,343	651.3	650.7	......
					217.3	12,960	1,938.5	1,936	......
					17.98	4,350	652.4	651.1	+0.05
Nov. 26..	2.12	7.20	......	7.09	18.00	4,505	675.7	674.8	......
					217.3	17,570	2,628	2,626	......
					18.00	4,513	676.8	675.5	+0.1
Nov. 27..	2.13	7.235	......	14.29	18.00	4,568	685.1	684.2	......
					217.9	19,760	2,956	2,953	......
					18.00	4,572	685.7	684.4	0
Nov. 28..	2.14	7.11	......	28.61	18.00	4,585	687.6	687.0	......
					218.1	21,515	3,219	3,216	......
					18.00	4,574	685.9	684.6	—0.35

*Experiments 2.3a and 2.3b were rejected, since the final conductance shows that some accidental contamination of the solution has occurred.

TABLE 78.—*Conductivity* ***data on ammonium*** *acetate*—Continued.

Date.	Experiment No.	Milli-equivalents per kilogram.			Temperature t°.	Conductance × 10⁶.	Specific conductance × 10⁶.		Percentage change at 18°.
		$NH_4C_2H_3O_2$	NH_4OH	$HC_2H_3O_2$			Uncorrected.	Corrected for impurities.	
1905									
Nov. 29..	2.15	14.20	......	......	18.00	8,548	1,282	1,281.5	......
					216.9	25,885	3,872	3,869	......
					18.00	8,558	1,283.5	1,282	+0.1
Nov. 30..	2.16	14.16	......	14.09	18.00	8,611	1,291.5	1,290.5	......
					217.9	33,885	5,069	5,066	......
					18.00	8,611	1,291.5	1,290	—0.05
Dec. 1..	2.17	14.165	......	28.04	18.00	8,656	1,298	1,297	......
					218.9	37,580	5,621	5,618	......
					18.00	8,639	1,295.5	1,294	—0.25
Dec. 2..	2.18	14.155	......	56.20	18.00	8,728	1,309	1,308	......
					218.2	41,305	6,179	6,176	......
					18.00	8,654	1,298	1,296.5	—0.9
1906									
Apr. 21..	2.19a	14.35	......	......	18.00	8,816	1,295	1,294.5	......
		14.195	......	......	304.8	5,818	851	845	......
		14.195	......	......	18.00	8,740	1,284	1,280.5	—1.1
Apr. 22..	2.19b	14.35	......	......	18.00	8,817	1,295.5	1,294.5	......
		14.28	......	......	304.9	5,849	855.5	849	......
		14.28	......	......	18.00	8,791	1,291.5	1,288	—0.5
Apr. 25..	2.20a	14.39	......	14.275	18.00	8,944	1,314	1,313.5	......
		14.18	......	14.275	304.3	8,310	1,215.5	1,209	......
		14.18	......	14.275	18.00	8,838	1,298.5	1,294.5	—1.5
Apr. 27..	2.20b	14.39	......	14.275	18.00	8,940	1,313.5	1,312.5	......
		14.205	......	14.275	304.6	8,264	1,209	1,202	......
		14.205	......	14.275	18.00	8,846	1,299.5	1,296	—1.3
May 4..	2.21	14.405	......	42.92	18.00	9,020	1,325	1,324.5	......
		14.075	......	42.92	305.1	11,175	1,634.5	1,628	......
		14.075	......	42.92	18.00	8,743	1,284.5	1,281	—3.3
May 30..	2.22	14.405	14.62	......	18.00	8,956	1,313.5	1,313	......
		14.275	11.68	......	305.0	7,753	1,132.5	1,127	......
		14.275	11.68	......	18.00	8,893	1,304.5	1,301	—0.9
June 2..	2.23a	14.315	42.39	......	18.00	9,024	1,323.5	1,323	......
June 3..	2.23b	13.90	36.02	......	305.2	10,385	1,517	1,511	......
		13.90	36.02	......	18.00	8,780	1,288	1,284.5	—2.9
June 23..	2.24a	43.13	......	......	18.00	24,150	3,695	3,694	......
		41.79	......	......	304.8	16,540	2,520	2,514	......
		41.79	......	......	18.00	23,470	3,591	3,587	—2.9
June 23..	*2.24b	43.13	......	......	18.00	24,130	3,692	3,691	......
		39.23	......	......	304.7	15,985	2,435	2,429	......
		39.23	......	......	18.00	22,125	3,385	3,381	—8.4
June 25..	2.24c	41.74	......	......	304.7	16,475	2,510	2,504	......
		41.74	......	......	18.00	23,435	3,586	3,582	—3.0
June 26..	2.25a	43.49	132.5	......	18.00	24,535	3,754	3,753	......
	2.25b	40.23	97.1	......	304.8	28,470	4,338	4,332	......
		40.23	97.1	......	18.00	22,840	3,495	3,491	—7.0
June 28..	2.26	43.52	......	45.35	18.00	24,540	3,751	3,750	......
		40.87	......	45.35	304.8	23,380	3,558	3,552	......
		40.87	......	45.35	18.00	23,180	3,543	3,539	—5.6
June 29..	3.1	43.81	......	125.9	18.00	24,455	3,738	3,737	......
		39.11	......	125.9	304.2	30,790	4,686	4,680	......
		39.11	......	125.9	18.00	22,030	3,367	3,363	-10.0

*The result at 306° from this experiment was rejected, because of its wide deviation from the others.

83. EQUIVALENT-CONDUCTANCE VALUES AT ROUND TEMPERATURES.

The next step in the further reduction of the data to comparable values is their correction to round temperatures. Temperature-coefficients at 18°, 218°, and 306° were obtained by plotting against the temperature the conductances given in the preceding tables after correcting them approximately to round concentrations. Thus the correction to round temperatures was made on the conductance alone, none being required on the concentration. In the case of ammonium hydroxide, the data obtained at 302°, before the use of diphenylamine as a heating substance was abandoned, permitted a more accurate calculation of the temperature-coefficient than could be obtained for 306° by drawing the curve through 156°, 218°, and 306°. Yet, since the correction to round temperatures was seldom more than 2 per cent, the coefficient does not need to be very accurately known.

In table 79 are given the temperature-coefficients employed, expressed in per cent of the equivalent conductance at the temperature in question for the first four substances, and in per cent of the specific conductance for ammonium acetate.

TABLE 79.—*Temperature-coefficients of conductance.*

Substance.	Milli-equivalents per liter.	18°.	218°.	306°.
NH_4Cl	30	2.20	......	0.16
	10	2.20	0.36	0.21
	2	2.20	0.37	0.26
$NaC_2H_3O_2$	30	......	......	0.20
	10	......	......	0.25
	2	......	......	0.32
NH_4OH	300	......	......	−2.65
	100	2.38	−0.78	−3.95
	10	2.15	−0.66	......
$HC_2H_3O_2$	300	......	......	−2.0
	100	1.70	−0.77	−3.0
$NH_4C_2H_3O_2$	30	......	......	−3.15
	10	2.75	−0.85	−3.35
1 $NH_4C_2H_3O_2$ + 1 NH_4OH or 1 $HC_2H_3O_2$	30	......	......	−2.8
	10	2.75	−0.82	−2.95
1 $NH_4C_2H_3O_2$ + 3 NH_4OH or 3 $HC_2H_3O_2$	30	......	......	−2.3
	10	2.75	−0.77	−2.4

In table 80 are given the conductance values for ammonium chloride. The first column gives the number of the experiment, corresponding to that in the table of Conductivity Data. The next three columns give the concentration in milli-equivalents per liter of solution, calculated as described in section 80. The fifth column shows the ratio, in equivalents, of the ammonium hydroxide to the ammonium chloride present, the excess of base having been added in the experiments carried to the higher temperature in order to reduce the hydrolysis nearly to zero. The next three columns give the equivalent conductance at 18° before and after heating to 218° or 306°, and that at 218° or 306°. The increase of conductance at 18° shows that a slight contamination occurred. This has been corrected for in the last column by diminishing the conductance at 218° or 306° by one-half of the percentage increase at 18°. This correction is about 0.1 per cent, except in Nos. 1.2b and 1.8 where it is 0.5 per cent; the results of these experiments are therefore given a weight of one-half.

In table 81 are given in a similar manner the results with sodium acetate.

TABLE 80.—*Equivalent conductance of ammonium chloride at round temperatures.*

Experiment No.	Milli-equivalents of salt per liter.			Ratio of NH_4OH to NH_4Cl.	Equivalent conductance.			
	18° initial.	18° final.	218°		18° initial.	18° final.	218°	218° corrected.
1.5a	12.05	......	......	0	121.85	......	......	......
1.5b	12.05	......	......	0	121.9	......	......	......
1.1	10.885	......	......	0	122.2	......	......	......
1.6	2.252	......	......	0	126.3	......	......	......
2.0	12.065	12.10	10.22	0.49	122.15	122.2	757.6	757.4
1.4	10.015	10.045	8.48	0.60	122.85	123.05	765.4	764.6
1.2a	2.356	......	......	0.51	126.85	......	......	......
1.2b	2.356	2.363	1.995	0.51	126.9	128.15	802.3	798.3
1.3a	2.238	2.245	1.894	0.54	126.8	126.9	802.2	801.8
1.3b	2.238	2.245	1.895	0.54	127.25	127.35	804.1	803.7
			306°.				306°.	306° cor.
1.10	43.41	43.41	30.48	1.00	116.15	116.3	828	827.5
1.9	14.275	14.275	10.03	1.82	121.65	121.8	925.5	925
1.7	2.897	2.901	2.035	2.51	127.15	127.8	1,032	1,029.5
1.8	2.851	2.852	1.999	4.60	127.35	128.8	1,040.5	1,034.5
	25°.				25°.			
1.1	10.87	......	......	0	141.35	......	......	......
1.6	2.249	......	......	0	146.25	......	......	......

TABLE 81.—*Equivalent conductance of sodium acetate at round temperatures.*

Experiment No.	Milli-equivalents of salt per liter.		Ratio of $HC_2H_3O_2$ to $NaC_2H_3O_2$.	Equivalent conductance.		
	18°	306°		18° initial.	18° final.	306°.
1.4	42.52	29.95	1.07	66.85	66.8	613
1.3	14.13	9.92	1.56	71.3	71.1	702.5
1.1	2.844	1.998	2.62	75.3	75.55	800
1.2	2.806	1.9685	4.11	75.9	77.1	803

It will be seen that the conductances at 18° of the first four ammonium chloride solutions containing no excess of ammonia are uniformly about 0.3 per cent lower than those of the solutions containing ammonia. The cause of this small difference is not known; but it may be due to a slight contamination by carbon dioxide. It may also be mentioned that, when corrected to the same concentration, the conductance of ammonium chloride solution No. 2 which was made from standardized hydrochloric acid and ammonia, agrees almost exactly with that of the other entirely independent solutions made from the stock solution of the crystallized salt.

In tables 82 and 83 are presented in a similar manner the equivalent conductances of acetic acid and ammonium hydroxide corrected for the impurities in the water and reduced to round temperatures. Two columns are, however, added in which are given the ionization-constants K_B or K_A for these substances calculated directly from the separate values of the equivalent conductance by the equation $\frac{\Lambda^2 C}{(\Lambda_0 - \Lambda)\Lambda_0} = K_B$ or K_A; for this furnishes the best means of showing the agreement of the results of the different measurements. The Λ_0 values employed are those derived and tabulated in section 84. In the case of the experiments with ammonium hydroxide, solutions 1, 2, 3, 6, and 12 were prepared from Baker and Adamson's purest aqua-ammonia, the others from liquid ammonia, as described in section 78.

TABLE 82.—*Equivalent conductance and ionization-constant of acetic acid at round temperatures.*

Experiment No.	Milli-equivalents per liter.			Equivalent conductance.			$K_A \times 10^6$	
	18° initial.	18° final.	218°	18° initial.	18° final.	218°	18°.	218°
4	210.0	......	......	3.234	......	......	18.30	......
2	109.05	......	......	4.484	......	......	18.33	......
3a	97.45	......	......	4.747	......	......	18.37	......
1	91.3	......	......	4.920	......	......	18.50	......
3b	97.45	96.95	81.75	4.737	4.722	5.332	18.29	1.720
3c	97.45	96.9	81.75	4.731	4.733	5.340	18.25	1.725
Mean	......	......	......	......	......	......	*18.34	1.723
			306°			306°		306°
6a	433.5	432.3	300.4	2.198	2.154	0.836	17.39	0.1305
6b	433.5	432.2	299.2	2.198	2.156	0.843	17.39	0.1325
6c	433.5	432.3	292.7	2.200	2.160	0.852	17.42	0.132
6d	433.5	431.8	291.5	2.197	2.159	0.857	17.38	0.1335
Mean	......	......	......	......	......	......	17.40	0.132
5.1a	143.5	144.45	100.75	3.921	3.833	1.577	18.41	0.156
5.1b	143.5	144.15	100.4	3.920	3.844	1.563	18.40	0.153
5.1c	143.5	142.7	99.45	3.918	3.868	1.552	18.38	0.149
Mean	......	......	......	......	......	......	*18.40	0.153

*The mean of all the values at 18° for the concentrations between 210 and 91 milli-normal is 18.36.

TABLE 83.—*Equivalent conductance and ionization-constant of ammonium hydroxide at round temperatures.*

Experiment No.	Milli-equivalents per liter.			Equivalent conductance.			$K_B \times 10^6$	
	18° initial.	18° final.	218°	18° initial.	18° final.	218°	18°	218°
2a	103.2	......	......	3.051	......	......	17.13	......
2b	103.2	......	......	3.050	......	......	17.11	......
2c	103.2	......	......	3.051	......	......	17.13	......
2d	103.2	......	......	3.050	......	......	17.11	......
1a	99.7	......	......	3.109	......	......	17.18	......
1b	99.7	......	......	3.108	......	......	17.17	......
3	89.4	......	......	3.287	......	......	17.24	......
6	85.75	......	......	3.352	......	......	17.20	......
Mean	......	......	......	......	......	......	17.16	......
5b	106.6	......	......	3.003	......	......	17.13	......
5a	106.6	105.55	89.0	3.005	2.997	5.110	17.15	1.797
5c	106.6	105.1	89.55	3.000	2.998	5.096	17.09	1.794
5d	106.6	105.35	89.8	3.005	2.989	5.073	17.15	1.783
4	93.85	92.7	78.2	3.206	3.209	5.458	17.20	1.798
7a	89.75	......	......	3.281	......	......	17.23	......
7b	89.75	88.75	75.8	3.278	3.258	5.557	17.20	1.807
Mean	......	......	......	......	......	......	17.16	1.796
9.4	13.615	12.34	10.42	8.34	8.64	15.08	17.26	1.84
9.2	12.685	12.16	10.26	8.60	8.72	15.31	17.13	1.87
9.3	12.63	10.955	9.255	8.64	9.38	16.36	17.21	1.93
9.1a	10.495	......	......	9.41	......	......	17.02	......
9.1b	10.495	9.70	8.185	9.43	9.63	16.76	17.09	1.79
6.2	10.155	9.77	8.255	9.58	9.66	17.19	17.08	1.90
6.1	9.335	8.95	7.56	9.98	10.22	18.44	17.08	2.00
Mean	......	......	......	......	......	......	17.12	1.89
			306°			306°		306°
11	520.0	......	......	1.295	......	......	15.44	......
12	510.1	459.9	319.4	1.315	1.363	0.760	15.60	0.0935
13b	418.9	414.9	285.7	1.462	1.444	0.807	15.84	0.0940
13a	418.9	414.3	285.1	1.461	1.445	0.797	15.82	0.0915
13c	418.9	411.9	284.4	1.465	1.453	0.814	15.91	0.0955
Mean	......	......	......	......	......	......	......	0.0935
10b	147.2	......	......	2.546	......	......	16.97	......
8	146.1	......	......	2.558	......	......	17.00	......
9	134.25	......	......	2.671	......	......	17.04	......
13.1a	144.85	138.5	96.2	2.556	2.571	1.357	16.83	0.0895
13.1b	144.85	137.65	95.75	2.549	2.590	1.356	16.74	0.0890
10a	147.2	133.8	93.8	2.547	2.698	1.374	16.98	0.0895
10c	147.2	126.1	80.85	2.544	2.723	1.483	16.94	0.0900
10e	147.2	97.75	68.55	2.544	*3.636	1.598	16.94	0.0885
10d	147.2	97.0	61.7	2.546	3.195	1.681	16.97	0.0885
Mean	......	......	......	......	......	......	16.93	0.0895
	25°			25°			25°	
10e	147.0	......	......	2.963	......	......	17.82	......
9	134.0	......	......	3.115	......	......	17.96	......
Mean	......	......	......	......	......	......	17.89	......

*This was the conductance at 25°.

A comparison of the separate values of the ionization-constants for nearly the same concentrations in tables 82 and 83 shows at each temperature an entirely satisfactory agreement. Moreover, the mean of the first series of values for ammonium hydroxide, which were obtained with solutions prepared from a pure commercial aqua ammonia, will be seen to be identical with the mean of the second series of values, which with solutions prepared from a pure commercial aqua ammonia, will be

84. FINAL VALUES OF THE EQUIVALENT CONDUCTANCE AND THEIR VARIATION WITH THE CONCENTRATION AND TEMPERATURE.

Final values of the equivalent conductance at round concentrations for ammonium chloride and sodium acetate and for ammonium hydroxide and acetic acid have been derived from those given in tables 80 to 83.

This has been done in the case of the two salts at 306° with the help of the function $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$ by first determining the values of the three constants Λ_0, K, and n, by substituting the values of Λ at the three widely different concentrations, and then calculating in the reverse way the value of Λ for various round concentrations. In the case of ammonium chloride at 18° and 218°, however, since only two widely different concentrations were investigated, the value of n was assumed to be identical with that found for the very analogous salt potassium chloride, namely 1.42 at 18° and 1.50 at 218°. (At 18° and 25° the measurements with the pure salt, without excess of ammonium hydroxide, were alone utilized.) The values of Λ and of Λ_0 so obtained are summarized in Table 84. The values of n at 306° derived as just described are 1.44 for ammonium chloride and 1.49 for sodium acetate.

In the cases of ammonium hydroxide and acetic acid values for Λ_0 were first obtained indirectly by the relations:

$$\Lambda_{0(\mathrm{NH_4OH})} = \Lambda_{0(\mathrm{NH_4Cl})} + \Lambda_{0(\mathrm{NaOH})} - \Lambda_{0(\mathrm{NaCl})}$$
$$\Lambda_{0(\mathrm{HAc})} = \Lambda_{0(\mathrm{NaAc})} + \Lambda_{0(\mathrm{HCl})} - \Lambda_{0(\mathrm{NaCl})}$$

Most of the Λ_0-values for the substances on the right were taken from the various parts of this publication. In the case of sodium hydroxide, however, no measurements exist at 306°, and those at 218° are not sufficiently accurate nor extensive. Λ_0-values for it were therefore derived under the assumption that it lies at such a proportional distance between the Λ_0-values for sodium chloride and hydrochloric acid at these temperatures as is indicated by its position between them at the lower temperatures of 18°, 100°, and 156°. All these Λ_0-values are given in the following table. Those for ammonium acetate which are needed in the subsequent calculation of the hydrolysis of this salt are also included. They were derived by combination of those for ammonium chloride, sodium acetate, and sodium chloride. The Roman numerals within parentheses show the Part of this publication, and the immediately following number, the table, from which the Λ_0 values were taken.

Substance.	18°	25°	218°	306°
NH_4Cl.........	130.9*	152.0 (VII, 84)	841 (VII, 84)	1,176 (VII, 84)
$NaC_2H_3O_2$ ...	78.1 (V, 36)	......	660 (V, 36)	924 (VII, 84)
NaOH.........	216.5 (VI, 59)	......	1,060	1,310
HCl............	379 (V, 36)	......	1,265 (V, 36)	1,424 (VIII, 109)
NaCl..........	109.0†	......	760 (II, 9)	1,080 (II, 9)
NH_4OH	238.4	270.6‡	1,141	1,406
$HC_2H_3O_2$	348.1	......	1,165	1,268
$NH_4C_2H_3O_2$.	100.0	......	741	1,020

*Mean of the results presented in this Part, Table 84, and in Part VI, Table 59.

†Value of Kohlrausch.

‡Calculated from the NH_4OH value at 18° by means of Kohlrausch's temperature-coefficients for the ions (Sitzungsber. preuss. Akad., 1901, 1031).

With the help of these Λ_0-values for the ammonium hydroxide and acetic acid the ionization-constants $\frac{(C\Lambda)^2}{C(\Lambda_0 - \Lambda)\Lambda_0}$ already given in tables 82 and 83 were calculated; and from the means of these for each near-lying series of concentrations, the values of Λ at round concentrations were obtained by reverse calculation. The latter are summarized in table 84.

TABLE 84.—*Final values of the equivalent conductance at round temperatures.*

Substance.	Milli-equivalents per liter.	18°.	25°.	218°.	306°.
Ammonium chloride	30	118.1	......	......	828
	10	122.5	141.7	758	925
	2	126.5	146.5	801	1031
	0	131.1	152.0	841	1176
Sodium acetate	30	......	......	......	613
	10	......	......	......	702
	2	......	......	......	801
	0	......	......	......	924
Ammonium hydroxide	500	1.325	......	......	......
	300	1.752	......	......	0.785
	100	3.103	3.62	4.821	1.329
	80	3.466	......	5.389	......
	10	9.66	......	15.56	......
	0	238.4	270.6	1141	1406
Acetic acid	300	2.682	......	......	0.841
	100	4.685	......	4.824	1.567
	80	5.234	......	5.393	......
	0	348.1	......	1165	1268

For the sake of comparison the values obtained by other workers in this laboratory are here tabulated.

	0.002 Normal NH_4Cl at 18°.	0.1 normal NH_4OH.		0.08 normal $HC_2H_3O_2$.	
		at 18°.	at 25°.	at 18°.	at 218°.
Noyes and Cooper.	......	......	......	5.22	5.34
Noyes and Kato...	126.6	3.10	......	......	......
Kanolt	......	3.11	3.61	......	......
Sosman	*126.5	3.10	3.62	5.23	5.39

*Kohlrausch found 126.2.

It is of interest to consider the change with the temperature of the Λ_0-values for ammonium chloride and sodium acetate, taken in combination with the results of Noyes and Kato (table 59, Part VI) and of Noyes and Cooper, table 40, Part V). The values of $\Delta\Lambda/\Delta t$ for the successive temperature-intervals are given in table 85; and the ratio of their Λ_0-values to those of potassium chloride and sodium chloride at the same temperature are given in table 86.

TABLE 85.—*Temperature-coefficients of the equivalent conductance at zero concentration* ($\Delta\Lambda_0/\Delta t$).

Substance.	Λ_0 at 18°.	18–100°.	100–156°.	156–218°.	218–306°.
NH_4Cl............	130.9	3.47	3.80	3.43	3.81
$NaC_2H_8O_2$......	78.1	2.53	2.95	3.40	3.00

TABLE 86.—*Ratio of Λ_0-values to those for other substances.*

Substance.	18°.	100°.	156°.	218°.	306°.
$NH_4Cl : KCl$..............	1.01	1.00	1.00	1.02	1.05
$NaC_2H_8O_2 : KCl$........	0.60	0.69	0.72	0.80	0.82
$NaC_2H_3O_2 : NaCl$......	0.72	0.79	0.81	0.87	0.86

It will be seen from these tables that the Λ_0-values for ammonium chloride increase with the temperature in nearly the same way as do those for potassium chloride, there being two points of inflexion in the conductance-temperature curve, namely, between 100° and 218°, and 218° and 306°. For sodium acetate, on the contrary, the rate of increase with the temperature becomes steadily greater up to 218°. The equivalent conductance of the acetate ion, however, steadily approaches that of the chloride ion (except through the interval 218°–306° where the slight decrease in the ratio for sodium acetate to sodium chloride may be due to error).

With respect to the change of equivalent conductance with the concentration, mention need only be made of the fact that the values of the exponent n in the function $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$ are about the same for these two salts at 306° as for the other salts previously investigated, namely, 1.44 for ammonium chloride and 1.49 for sodium acetate. In the cases of the base and acid the value of n is approximately 2, as the mass-action law requires (see section 85).

The equivalent-conductance values for the base and acid (for example, at 100 milli-normal) decrease greatly between 218° and 306° and are less at the latter temperature than at 18°. This arises, of course, from a greatly decreased ionization, which overcompensates the increased equivalent conductance of the ions.

85. IONIZATION VALUES AND THEIR VARIATION WITH THE CONCENTRATION AND TEMPERATURE.

Table 87 contains the percentage ionization-values for the four substances whose equivalent conductances were given in table 84. These values are simply those of the ratios $100\Lambda/\Lambda_0$.

TABLE 87.—*Percentage ionization.*

Substance.	Milli-equivalents per liter.	18°.	25°.	218°.	306°.
Ammonium chloride	30	90.1	......	......	70.4
	10	93.5	93.2	90.1	78.7
	2	96.5	96.4	95.3	87.7
Sodium acetate	30	......	......	......	66.4
	10	......	......	......	76.0
	2	......	......	......	86.7
Ammonium hydroxide	500	0.556	......	......	......
	300	0.735	......	......	0.0558
	100	1.302	1.338	0.422	0.095
	80	1.454	......	0.472	......
	10	4.05	......	1.36	......
Acetic acid	300	0.771	......	......	0.0663
	100	1.346	......	0.414	0.124
	80	1.504	......	0.463	......

The ionization values for ammonium chloride and sodium acetate even at 306° are only slightly less than those for sodium and potassium chlorides, for which in 10 milli-normal solution the values 79.6 and 81.2 per cent were found by Noyes and Coolidge (see table 12, Part II). The ionization of both ammonium hydroxide and acetic acid is seen to have become very much less at the higher temperatures. The separate values of their ionization-constants have already been given in tables 82 and 83.

In table 88 are given the means of these for each group of nearly equal concentrations, which means correspond to the ionization values given in table 87. In computing these constants the concentration has been expressed in equivalents per liter. In the last line under each substance are given in black type, what are probably the best values for dilute solutions, taking into consideration the experimental errors in the more dilute solutions and the deviation from the mass-action law in the more concentrated ones.

TABLE 88.—*Ionization-constants* × 10⁶ *for ammonium hydroxide and acetic acid.*

Substance.	Equivalents per liter.	18°.	25°.	218°.	306°.
Ammonium hydroxide	0.52	15.5	......	......	......
	0.42	15.9	......	......	......
	0.30	......	......	......	0.094
	0.15	16.9	17.9	......	......
	0.10	17.2	......	1.80	0.090
	0.01	17.1	......	1.89	......
	Best Value	**17.2**	**18.1**	**1.80**	**0.093**
Acetic acid	0.43	17.4	......	......	......
	0.30	......	......	......	0.132
	0.14	18.4	......	......	......
	0.10	18.3	......	1.72	0.153
	Best Value	**18.2**	......	**1.72**	**0.139**

It will be noted that at 18° the ionization constants of both substances are considerably less at 0.4 normal than at 0.1 normal, doubtless because of inaccuracy in the assumptions involved — the validity of the mass-action law or the proportionality between ionization and equivalent conductance. That at the higher temperatures of 218° and 306° the mass-action law holds, at any rate approximately, at moderate concentrations is shown for ammonium hydroxide by these results. This has previously been shown to be true for acetic acid at 218° by Noyes and Cooper. Their values of the constant (18.2 and 1.69 × 10^{-6}) also agree well with mine (18.4 and 1.72 × 10^{-6}). This is especially true when the somewhat different manner of correcting for the conductance of the water is considered; thus their value at 218° when corrected as described in section 79 of this part becomes 1.72.

86. HYDROLYSIS OF AMMONIUM ACETATE AND IONIZATION OF WATER AT 218° AND 306°.

In order to derive the degree of hydrolysis of ammonium acetate, the specific-conductance values given in table 78 have been first corrected to round temperatures by means of the temperature-coefficients given in table 79, and the content by weight has been reduced in the usual way to volume-concentration at the temperature of the measurement. These conductance values were previously corrected for the conductance of the impurities in the water; and a correction has now been applied for that of the ionized water, or of the base or acid added, in those cases where the correction exceeds 0.1 per cent. This correction was calculated from the ionization-constants for these substances and the equivalent conductance of the ions, as described in section 79. In no case did the correction exceed 0.25 per cent.

Table 89 contains the so-corrected data for the pure salt, and table 90 those for the salt with an excess of base or acid. In the latter table are given for 218° and 306° in two additional columns (1) the specific conductance ($\underline{L}_0$) which the pure salt has at the same concentration as that (C) of the salt in the mixture, and (2) the ratio of the specific conductance ($\underline{L}$) of the salt in the mixture to this conductance $\underline{L}_0$. The specific conductance $\underline{L}_0$ is calculated from that given in table 89 for nearly the same concentration under the assumption of proportionality between conductance and concentration through the small interval involved.

TABLE 89.—*Specific conductance at round temperatures of pure ammonium acetate solutions.*

Experiment No.	Milli-equivalents per liter.			Specific conductance × 10^6.		
	18°.	218°.	306°.	18°.	218°.	306°.
1.3	14.57	......	......	1,311.5	......	......
1.4	14.44	......	......	1,302	......	......
2.1	14.01	11.81	......	1,266	3,770	......
2.15	14.18	12.01	......	1,281.5	3,830	......
Mean .	14.30	11.91	......	1,290	3,800	......
2.2	7.10	5.93	......	656.0	1,918.5	......
2.10	7.11	6.025	......	657.0	1,944.5	......
2.11	7.045	5.96	......	651.0	1,921.5	......
Mean .	7.085	5.97	......	654.7	1,928	......
2.24b	43.10	......	......	3,691	......	......
2.24a	43.10	......	29.38	3,694	......	2,412
2.24c	43.10	......	29.32	......	......	2,394
Mean .	43.10	......	29.35	3,693	......	2,403
2.19a	14.335	......	9.97	1,294.5	......	812
2.19b	14.335	......	10.015	1,294.5	......	818
Mean .	14.335	......	9.995	1,294.5	......	815

TABLE 90.—*Specific conductance at round temperatures of ammonium acetate solutions containing ammonium hydroxide or acetic acid.*

Temperature.	Experiment No.	Milli-equivalents per liter.		Specific conductance × 10⁶.		
		Salt in mixture.	Acid (A) or base (B).	Salt in mixture.	Salt in water alone.	Ratio.
$t°$		$C \times 10^3$	C_A or $C_B \times 10^3$	$L \times 10^6$	$L_0 \times 10^6$	L/L_0
218	2.16	11.94	11.88 A	5,057	3,809	1.328
	2.7	12.015	12.075 B	5,010	3,833	1.307
	2.17	11.90	23.61 A	5,651	3,797	1.488
	2.8	11.92	23.41 B	5,482	3,803	1.442
	2.18	11.825	47.38 A	6,173	3,773	1.636
	2.9	11.875	46.75 B	6,093	3,789	1.608
	2.12	6.08	5.985 A	2,606	1,963	1.328
	2.4a	6.00	6.25 B	2,563	1,944	1.318
	2.4b	6.04	6.25 B	2,562		
	2.13	6.10	12.055 A	2,944	1,969	1.495
	2.5a	6.025	11.78 B	2,875	1,944	1.476
	2.5b	6.015	11.78 B	2,863		
	2.14	5.975	24.12 A	3,207	1,930	1.662
	2.6	6.015	23.62 A	3,150	1,942	1.622
306	2.26	28.76	31.91 A	3,430	2,355	1.457
	3.1	27.53	88.6 A	4,482	2,254	1.988
	2.25	28.34	68.4 B	4,210	2,320	1.815
	2.20a	9.96	10.025 A	1,146	813	1.412
	2.20b	9.965	10.01 A	1,150		
	2.22	10.01	8.19 B	1,092	816	1.338
	2.21	9.855	30.06 A	1,589	803	1.979
	2.23	9.735	25.22 B	1,480	794	1.864

From the data given in table 90 the hydrolysis of the salt at 218° and at 306° has been calculated in two different ways.

The first of these is that used by Noyes and Kato (section 73, Part VI) in connection with their hydrolysis experiments at 156°. In this method, the following expressions for hydrolysis equilibrium and for the empirical relation of van't Hoff between the ionization and concentration of salts are combined:

$$\left(\frac{L}{L_0}\right)^2 = \frac{h\left(h + \frac{C_B}{C}\right)}{h_0^{\,2}}$$

$$\left(\frac{L}{L_0}\right)^{\frac{3}{2}} = \frac{1 - h - \frac{10^3 L}{C\Lambda_0}}{1 - h_0 - \frac{10^3 L_0}{C\Lambda_0}}$$

and thereby the values of h_0 and h, the hydrolysis of the salt at concentration C in pure water and in the mixture respectively, are calculated. Λ_0 is the equivalent conductance of completely ionized ammonium acetate; its values are 741 at 218° and 1020 at 306° (see section 84).

In the second method the ion-concentration is, as before, calculated by dividing the specific conductance of the solution (multiplied by 10^3) by the equivalent conductance of the completely ionized salt; and then the concentration of the un-ionized salt is estimated under the assumption that it has the same value as in a solution of an ordinary unhydrolyzed salt of the same ionic type at the same ionic concentration. Then merely by subtracting the un-ionized fraction (u) and the ionized fraction (γ) from unity, the hydrolyzed fraction (h) is obtained; that is, $h = 1 - \gamma - u$. In this calculation the mean ionization of potassium and sodium chlorides as determined by Noyes and Coolidge (table 12, Part II) was used as a basis. This calculation can give accurate hydrolysis values only when the hydrolyzed fraction is large and the un-ionized fraction very small; but under such conditions, which are in fact realized in the foregoing experiments fairly well at 218° and in much higher degree at 306°, it is the most direct method and a fairly reliable one. For example, suppose the hydrolyzed, ionized, and un-ionized parts were 80 per cent, 18 per cent, and 2 per cent respectively; then an error of even 3 per cent in the ionized, and of 25 per cent in the estimated un-ionized fraction, would make, if they lay in the same direction, an error of only one per cent in the hydrolyzed fraction.*

Table 91 contains the results of the calculations. In the fifth and sixth columns are given the values of the percentage hydrolysis ($100h$) calculated by the first and second methods, respectively. In the seventh column is given a mean derived from these. Since the results by the second method are more accurate the greater the hydrolysis, in deriving this mean a weight has been assigned to them equal to the percentage hydrolysis, the results by the first method being always given a weight of 100. It is desirable to combine the results by the two methods in some such way as this, since any error in the conductance ratio L/L_0 influences them in opposite directions. In the last three columns of the table are given the values of the percentage hydrolysis ($100\ h_0$) of the salt in pure water at the same concentration C. The values in the first of these columns are derived by the first method simultaneously with those of $100\ h$. Those in the second of these columns are calculated from the mean value of $100h$ given in the seventh column by the equation $h_0^2 = \dfrac{h(h + C_B/C)}{(\text{L}/\text{L}_0)^2}$. Those in the last column are obtained directly by the second method from the conductance in pure water.

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*The calculations were also made by still a third method, namely, that described by C. W. Kanolt in Section 103, Part IX, but in this case where the hydrolysis is very large the results were found to be much more influenced by the experimental error than those calculated by the first method. They are therefore not recorded here.

TABLE 91.—*Hydrolysis and ionization of ammonium acetate at 218° and 306°.*

Temperature. $t°$	Concentration of salt $C \times 10^3$	Concentration ratio $\frac{C_A}{C}$ or $\frac{C_B}{C}$	Salt in mixture.				Salt in pure water.			
			Ionization 100γ	Percentage hydrolysis ($100h$).			Ionization $100\gamma_0$	Percentage hydrolysis ($100 h_0$)		
				By first method.	By second method.	Weighted mean.		By first method.	From mean value of h.	By second method.
218	11.91	0	......	......	......	......	43.1	......	......	53.3
	11.94	0.995 A	57.2	35.5	37.4	36.0	43.1	52.1	52.6	......
	11.90	1.984 A	64.1	26.2	29.5	27.0	43.1	51.6	52.4	......
	11.825	4.007 A	70.5	16.5	22.3	17.6	43.1	50.7	51.7	......
	Mean ..	......	......	......	......	......	......	51.5	52.2	......
	12.015	1.005 B	56.3	29.6	38.4	32.0	43.1	47.5	49.8	......
	11.92	1.964 B	62.1	21.5	31.8	24.0	43.1	47.4	50.5	......
	11.875	3.937 B	69.2	15.5	23.7	17.1	43.1	49.5	52.1	......
	Mean ..	......	......	......	......	......	......	48.1	50.8	......
	5.97	0	......	......	......	......	43.6	......	......	53.7
	6.08	0.984 A	57.8	36.0	38.0	36.5	43.6	52.4	52.9	......
	6.10	1.976 A	65.1	27.1	30.0	27.8	43.6	52.2	52.9	......
	5.975	4.037 A	72.4	17.6	22.0	18.4	43.6	51.8	53.0	......
	Mean ..	......	......	......	......	......	......	52.1	52.9	......
	6.02	1.038 B	57.5	30.6	38.4	32.7	43.6	48.6	50.7	......
	6.02	1.957 B	64.3	25.2	30.9	26.5	43.6	50.6	52.0	......
	6.015	3.927 B	70.7	16.1	23.8	17.6	43.6	50.0	52.4	......
	Mean ..	......	......	......	......	......	......	49.7	51.7	......
306	29.35	0	......	......	......	......	8.03	......	......	90.9
	28.76	1.110 A	11.69	93.4	86.3	90.1	8.03	94.8	92.4	......
	27.53	3.218 A	15.96	81.2	81.0	81.1	8.03	91.0	90.9	......
	Mean ..	......	......	......	......	......	......	92.9	91.6	......
	28.34	2.414 B	14.56	85.0	82.8	84.0	8.03	91.8	91.1	......
	10.00	0	......	......	......	......	7.99	......	......	91.2
	9.965	1.006 A	11.29	90.2	87.5	88.9	7.99	92.9	91.9	......
	9.855	3.050 A	15.81	86.0	82.3	84.3	7.99	92.7	91.6	......
	Mean ..	......	......	......	......	......	......	92.8	91.7	......
	10.01	0.818 B	10.70	86.7	88.2	87.4	7.99	90.3	90.9	......
	9.735	2.591 B	14.91	85.8	83.4	84.7	7.99	92.3	91.5	......
	Mean ..	......	......	......	......	......	......	91.3	91.2	......

A comparison of the values of the percentage-hydrolysis ($100\,h$) of the salt in the mixture calculated by the two methods shows at 218° a considerable divergence, especially in the experiments where an excess of base was added. This was doubtless due largely to the destruction of some of the base during the heating. At 306° where this was determined and allowed for, and where the calculation by the second method is more accurate, the agreement is far more satisfactory (except in the first experiment which appears to be affected by some accidental error). From an examination of the values of the percentage hydrolysis ($100\,h_0$) of the salt in pure water it is seen that the experiments in which different quantities of acid were added gave very concordant results, whether calculated directly by the first method or from the weighted mean value of the percentage hydrolysis (100 h) for the salt in the mixture. The mean value calculated from the latter is, however, to be considered the most accurate. It will be seen that this agrees well in all cases with the value given in the last column, which was calculated directly by the second method from the conductance of the salt in pure water. To get the best final value from each group of experiments we have combined these two by assigning to the former a weight of 100 and to the latter a weight equal to the percentage hydrolysis. Table 92 contains the final hydrolysis values so obtained, the ionization values for the salt, the ionization-constant of water calculated from them by the equation $K_W = K_A K_B h_0^2/\gamma_0^2$, and the square root of the constant, which represents the concentration C_H of the hydrogen (or hydroxide) ion in pure water.

TABLE 92.—*Ionization of water at 218° and 306°.*

Temperature	Final results with ammonium acetate.			Ionization constant of water × 10¹⁴.	Equivalents of hydrogen-ion per 10⁷ liters
	Equivalents per liter.	Percentage ionization.	Percentage hydrolysis.		
$t°$	C	$100\gamma_0$	$100h_0$	$K_W \times 10^{14}$	$C_H \times 10^7$
218	0.012	43.1	52.6	461	21.5
	0.006	43.6	53.2	461	21.5
			Mean	461	21.5
306	0.030	8.03	91.3	167	12.9
	0.010	7.99	91.5	170	13.0
			Mean	168	13.0

A comparison of these values of the ionization-constant with those presented in Part VI by Noyes and Kato (48 at 100° and 223 at 156°) shows that the constant is considerably greater at 218° than at the lower temperatures, but that it has become much less at 306°. From a plot of the values it appears probable that the maximum lies between 250° and 275°.

87. SUMMARY.

In this article have been presented the results of conductivity measurements with ammonium hydroxide, acetic acid, and ammonium chloride at 18°, 218°, and 306°, and with sodium acetate at 306°. The final values of the equivalent conductance will be found in table 84, and of the corresponding ionization in table 87.

The equivalent conductance of completely ionized ammonium chloride, which at 18° is nearly equal to that of potassium chloride, becomes 2 per cent greater at 218° and 5 per cent greater at 306°; and that of sodium acetate, which at 18° is only 71 per cent of that of sodium chloride, becomes 86 per cent of it at 218° and 306°. The ionization of the two salts is at all temperatures only a little less than that of sodium and potassium chlorides; thus at 306° the differences are about 2 per cent and 4 per cent, respectively. The hydrolysis of these salts was not measured, but was reduced substantially to zero by the addition of an excess of the weak base or acid. Its value can, however, be calculated from the ionization-constants of water, ammonium hydroxide, and acetic acid determined in this research*; and it is of interest to note that in 0.01 normal solution both salts at 218° are 1.56 per cent hydrolyzed, and that at 306° ammonium chloride is 4.1 and sodium acetate 3.4 per cent hydrolyzed, while at 18° the hydrolysis is only 0.02 per cent.

The ionization of the slightly ionized substances, acetic acid and ammonium hydroxide, decreases with great rapidity as the higher temperatures are reached; thus the ionization-constants ($\times 10^6$), as determined from the measurements at 218° and 306° presented in this article and from the earlier ones at 18°, 100°, 156°, and 218° by Noyes and Cooper, and Noyes and Kato, are as follows:

	Acetic Acid.	Ammonium Hydroxide.
18°	18.3	17.2
100°	11.1	13.5
156°	5.42	6.28
218°	1.72	1.80
306°	0.139	0.093

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*These calculations were made, for sodium acetate for example, by the substantially exact mass-action relation $\frac{Ch^2\gamma_B}{(1-h)\gamma}=\frac{K_W}{K_A}$, wherein C represents the concentration of the salt, h the hydrolyzed fraction of it, γ the ionized fraction of the quantity of it unhydrolyzed $(C-Ch)$, γ_B the ionized fraction of the total quantity of free base (Ch), K_A the ionization-constant for the acid, and K_W that for water. For the ionized fractions γ and γ_B in the mixture may be taken the value for the pure salt and that for the pure base, respectively, when present alone at the concentration C, the principle being here applied that in a mixture of largely ionized substances the ionization of each is the same as if it were present alone at a concentration equal to the sum of the concentrations.

In this article have also been presented determinations of the degree of hydrolysis of ammonium acetate at 218° and 306°. This has been derived from measurements of the change in conductance produced when to the solution of the neutral salt acetic acid or ammonium hydroxide is added. In 0.01 normal solution the pure salt was found to be 53 per cent hydrolyzed at 218° and 91 per cent at 306°, while it can be shown by calculation to be only 0.35 per cent hydrolyzed at 18°; thus showing the enormous effect of temperature in increasing the hydrolysis of salts.

From the hydrolysis and ionization of the ammonium acetate and from the ionization-constants of the acid and base the ionization of water itself at 218° and 306° has been calculated. The final results together with those obtained at lower temperatures by the previous workers in this laboratory, are as follows. The values show the equivalents of hydrogen-ion or hydroxide-ion present in ten million liters of pure water.

100°	156°	218°	306°
6.9	14.9	21.5	13.0

The considerable increase between 100° and 218° and the decrease between 218° and 306°, indicating a maximum between these temperatures, will be noted.

PART VIII.

THE CONDUCTIVITY AND IONIZATION OF HYDROCHLORIC, NITRIC, AND SULPHURIC ACIDS UP TO 306°, AND OF PHOSPHORIC ACID AND BARIUM HYDROXIDE UP TO 156°.

BY ARTHUR A. NOYES AND GUY W. EASTMAN.

PART VIII.

THE CONDUCTIVITY AND IONIZATION OF HYDROCHLORIC, NITRIC, AND SULPHURIC ACIDS UP TO 306°, AND OF PHOSPHORIC ACID AND BARIUM HYDROXIDE UP TO 156°.

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88. OUTLINE OF THE INVESTIGATION.

In this article, after a brief description of experimental details, are given the results of conductivity measurements with aqueous solutions of sulphuric, phosphoric, and nitric acids, and barium hydroxide at various concentrations at temperatures up to 156°. The measurements were for the most part made at 18°, 25°, 50°, 75°, 100°, 128°, and 156°, and at the concentrations 100, 50, 12.5, 2, and 0.5 milli-normal. Conductivity measurements with nitric and sulphuric acids at the still higher temperatures of 218° and 306°, and with hydrochloric acid at 260° and 306° were also made, and these are included with the others. Some results with sulphuric acid extending up to 218° which were obtained somewhat earlier in this laboratory by Mr. Yogoro Kato are also here presented in conjunction with our own.

Finally, the results are all discussed with reference to the ionization of the various substances and the equivalent conductance of their ions at different temperatures.

89. DESCRIPTION OF THE APPARATUS AND METHOD.

CONDUCTIVITY-VESSEL.

The conductivity bomb (No. 1) employed in most of this work, was the first one made in this laboratory as described in Part II of this series. It had been used just previously by Mr. Yogoro Kato for the investigation described in Part VI and for his measurements with sulphuric acid presented below. It then contained an open cylindrical platinum-iridium electrode arranged as shown in figure 13, Part III; and in that form will be designated Cell I below. For our experiments this electrode was replaced by a flat platinum-iridium electrode placed at the bottom of a quartz cup, 1.45 cm. in height and 1.40 cm. in diameter. The vessel in this form will be called Cell II. For some of our later measurements another bomb (No. 3) with a similar electrode was used, the quartz cup in which was 1.40 cm. in height and 1.37 cm. in diameter. This will be called Cell III.

CONDUCTIVITY MEASURING APPARATUS AND INDUCTOR.

A slide-wire bridge of the roller type, described by Kohlrausch and Holborn, and made by Hartmann and Braun, was used to measure the conductance. The coils were of manganine and of 1, 10, 100, 1,000, and 10,000 ohms resistance. Each coil was compared directly in the Institute's testing laboratory with manganine standards having the Reichsanstalt seal and certificate. The slide-wire was calibrated twice by the method of Strouhal and Barus. The corrections both to the coils and slide wire agreed within the experimental error with the results of Kato obtained a few months earlier.

An ordinary interrupter was used. The minimum sound in the telephone was very good except for the most dilute and most concentrated solutions, and fairly good for them.

HEATERS.

For the work up to and including 156°, a liquid bath of pseudocumene, heated electrically by an inside and outside coil, and well stirred, was used. Cooling was effected by running tap water through a copper coil immersed in the bath. The temperature was regulated by the observer, by varying the current through the coils. It could be held at a desired temperature within the negligible variations of 0.02° at 18° and 0.1° at 156°.

For the temperatures of 218°, 260°, and 306° vapor baths of boiling naphthalene, isoamyl benzoate, and benzophenone, respectively, were used.

THERMOMETERS.

Up to and including 100°, mercury thermometers graduated in tenths of a degree were used. Since stem exposure could not always be avoided, they were calibrated in position as used by comparison with a standard Baudin thermometer, having a Bureau of Standards' certificate. The ice and steam readings remained substantially constant throughout the work. The error in the bath temperature could hardly have exceeded 0.02° at the 18°, 25°, 50°, and 100° points, but at 75°, owing to the necessity for applying a large stem-exposure correction to the standard Baudin, the error may have been as much as 0.05°. The temperatures above 100° were probably determined with an accuracy of 0.2° – 0.3°. At these temperatures a 360° Alvergniat thermometer, graduated in degrees, was used. The ice, steam, naphthalene, and benzophenone points were directly determined. Intermediate corrections were computed for 128° and 156° from the bore calibration, allowing for deviations of the mercury from the gas scale, as given by Crafts.* The correction at 260° was determined by comparison with a platinum resistance thermometer which had been standardized in this laboratory by Mr. R. D. Mailey. The values used for the boiling points of naphthalene and benzophenone were those of Jacquerod and Wassmer;† namely, at a pressure of 76 cm. mercury, 217.7° for the former substance and 305.44° for the latter.

METHOD OF PROCEDURE.

No important change in the method of procedure as described in Part IV was made. The contents of the bomb were always well shaken within the bath by rotating the bomb several times before and between the readings. Constant uniform temperature was thus quickly obtained, and any contamination in the quartz cup distributed through the whole solution. In the measurements up to 156° the bomb was filled from a pipette with such a quantity of solution that the vapor space at 156° was about 7 c.cm. In those extended to still higher temperatures such a quantity of solution was always placed in the bomb as sufficed to fill it within 2 or 3 c.cm. at the highest temperature of the experiment in question. The solutions were always placed in the bomb the day they were made up from the stock solution.

Only after the temperature of the bath had remained constant for at least 15 minutes were final bridge-readings taken; then at five minute intervals, double settings (reversing the commutator) were made with each of three different resistances in the box. Before introducing the most dilute solution of any substance, the bomb was first soaked out by heating with conductivity water or the solution itself to 218° or 306°. The solutions successively introduced into the bomb were then always of increasing conductance. Washing with alcohol and ether was avoided as far as possible, as their use seemed to be always followed by greater differences than usual between the initial and final 18° conductances.

90. PREPARATION OF THE SUBSTANCES AND SOLUTIONS.

The potassium chloride used for determining the conductance-capacity of the bomb was made from J. T. Baker's "Analyzed C. P." salt, said to contain only "traces" of magnesium and of sodium chlorides. This was precipitated from solution with hydrochloric acid and then showed no flame test for sodium. This precipitated salt was washed with hydro-

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*Am. Chem. J., **5**, 307-338 (1883-84). A check on these corrections was obtained by comparing the correction at 218° computed from the bore calibration and the steam and benzophenone determinations, with the actually observed correction in the naphthalene bath. The results agreed within 0.1°. A further check was obtained some months later by comparison with a certified German thermometer divided in tenths, between 100° and 200°, the greatest discrepancy being 0.2°.

†J. chim. phys., **2**, 72 (1904).

chloric acid, dried, dissolved in boiling water, and crystallized at 5°. The crystals were washed and dried. A second sample was obtained by adding hydrochloric acid to the mother liquor from these crystals. No difference was noticed in the conductances of these two lots. In making standard solutions this substance was freshly ignited almost to the fusing point, weighed out, and dissolved in a graduated flask.

Sodium chloride was also used for determining the conductance-capacity. This was purified by twice precipitating Kahlbaum's "chemically pure" product with hydrochloric acid. The final precipitate was dried and gently ignited.

The stock sulphuric acid solution used for all the measurements was a fifth-normal one prepared by Mr. Y. Kato on August 10, 1905, by diluting with conductivity water a sample of the "strictly chemically pure sulphuric acid" furnished by Baker and Adamson. The concentrated acid (usually 10 c.cm. portions) was tested by him for arsenic with hydrogen sulphide, for nitric acid with diphenylamine, for nitrous acid with starch and potassium iodide, for hydrochloric acid with silver nitrate, for selenium with ferrous sulphate, and for ammonia with Nessler solution. None of these impurities was present in appreciable quantity, if at all. The concentration of the solution was determined on August 11–15, 1905, both by precipitating and weighing the acid as $BaSO_4$ and by titration with phenolphthalein against a hydrochloric acid solution previously standardized by weighing the AgCl yielded by it. The sulphuric acid was restandardized on December 9, 1905, against an ignited sample of sodium carbonate furnished with an analysis showing substantial purity by J. T. Baker.* To the solution of a known weight of the carbonate, a slight excess of the stock sulphuric acid was added, the solution boiled for ten minutes and then titrated with 0.01 normal potassium hydroxide with the help of phenolphthalein as an indicator.

We are indebted to Mr. G. A. Abbott for the preparation and analysis of the stock solution of phosphoric acid which was used in this part of the investigation. This sample of acid was prepared by Mr. Abbott by direct oxidation of yellow phosphorus. The method is summarized as follows: Carefully selected clean pieces were heated in a retort with nitric acid (sp. gr. 1.20). After the phosphorus had disappeared the contents of the retort were evaporated in small portions with addition of enough nitric acid to insure complete oxidation of any phosphorous acid until the white fumes of metaphosphoric acid appeared. The cooled residue was taken up in conductivity water and saturated with hydrogen sulphide, in order to precipitate possible traces of arsenic or platinum. The metaphosphoric acid solution thus obtained was converted to the ortho acid by boiling in a platinum dish for three hours. That the conversion in this solution was complete was shown by the fact that the conductance of the diluter solutions prepared from it was not changed by heating to 156°.

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*The $BaSO_4$ determinations gave for the concentration, expressed in millimols H_2SO_4 in a kilogram of solution, 110.54, 110.51, and 110.52, from which by correcting the weighings to vacuo, the value 110.43 results. The atomic weights used were $O = 16.00$, $Ba = 137.4$, $S = 32.06$, and $H = 1.01$. By the titration against the hydrochloric acid the value 110.70 was obtained; and from that against sodium carbonate 110.71 resulted. The mean 110.61 was adopted.

The solution received January 17, 1906, from Mr. Abbott was part of a stock solution which he had analyzed gravimetrically by precipitating the phosphoric acid with magnesium ammonium chloride and weighing as magnesium pyrophosphate. The five analyses made by him gave as a mean value 20.0866 grams of H_3PO_4 per kilogram of solution. Assuming 1 mol $H_3PO_4 = 98.02$ grams, the concentration of this solution becomes 0.2049 mols per kilogram of solution.

The nitric acid solution was made by diluting a portion of "C. P. nitric acid," of specific gravity 1.42, taken from a newly opened carboy, with half as much water, bubbling through it for one day a current of carefully purified air, so as to remove nitrous acid, and finally diluting with enough conductivity water to give a very nearly 0.1 normal solution. The stronger solution was tested for nitrous,* sulphuric and hydrochloric acids, for ammonium salts (with Nessler reagent), and for non-volatile residue. None of these impurities were present in quantity as large as 0.01 per cent of the nitric acid present. The acid was standardized by comparison with the sulphuric acid solution just described through a 0.1 normal sodium hydroxide solution, and also directly against sodium carbonate. Its concentration was thus found to be 99.70 and 99.87 (mean 99.78) milli-equivalents per kilogram of solution.

The barium hydroxide used for preparing the stock solution of this substance was purified by twice crystallizing from hot water in procelain vessels a "chemically pure" preparation of Merck's. The crystals so obtained were dissolved in hot conductivity water, the solution filtered immediately out of contact with ordinary air, the filtrate allowed to run into about three liters of water of specific conductance 0.6×10^{-6} contained in a "Non-Sol" bottle (furnished by Whitall, Tatum & Co.). After standing for 24 hours, this solution, from which crystals separated on cooling, was forced over into a second "Non-Sol" bottle containing enough more conductivity water to dilute it to about 0.2 normal. The final solution was perfectly clear and remained so.

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*The test for nitrous acid was made by adding to 1 c.cm. of the stronger solution 100 c.cm. water, 10 c.cm. of an acetic acid solution of sulphanilic acid, and 10 c.cm. of a solution of naphthylamine acetate, and allowing the mixture to stand. For comparison a minute quantity of nitrite was added in a duplicate test. The result showed that, while one part of nitrous acid in a million could be detected, less than this was present in the strong nitric acid.

This solution was tested for chloride, and the original substance was tested for nitrate,* with negative results. That it contained no important quantity of non-volatile impurities was shown by precipitating the barium by running the solution into an excess of the stock sulphuric solution, allowing it to stand, filtering, and evaporating the filtrate first in a porcelain beaker and finally in a weighed platinum dish. The residue so obtained from 100 c.cm. of the cold-saturated barium hydroxide solution weighed 5.6 milligrams, of which only one milligram was shown to be silica by treatment with hydrofluoric acid. Some of the remainder was doubtless unprecipitated barium sulphate; but even if the whole of it had been an impurity in the barium hydroxide, it would not amount to more than 0.1 per cent.

A more conclusive test of purity of both the barium hydroxide and sulphuric acid was obtained as follows: 118.77 grams of the stock barium hydroxide solution were run into 113.38 grams of the stock sulphuric acid solution, previously heated to boiling. This should have left, according to computation, a slight excess of acid in the clear filtrate. The specific conductance of this filtrate was measured, and it was computed therefrom that assuming only sulphuric acid to be present an excess of 0.39 grams of its solution must have been added. Titration with 0.01 normal sodium hydroxide showed almost exactly the same quantity (0.42 grams), indicating that not enough impurity was present to affect appreciably the measured conductance.

This last experiment evidently gives also a means of comparing the stock solution of barium hydroxide with that of sulphuric acid, and thus tying together the whole series of values. The concentration of the barium hydroxide, so computed, is 0.17 per cent less than the adopted value, a difference not greater than the discrepancies in the analyses by independent methods of the same solution.

The concentration of the stock solution of barium hydroxide was found on March 20, 1906, by means of three titrations against the stock nitric acid, using phenolphthalein as indicator, to be 210.83 milli-equivalents per kilogram of solution.

The stock solution of hydrochloric acid was made by bubbling the gas produced by the action of pure sulphuric acid on pure sodium chloride through a little water and then absorbing it in conductivity water. It was standardized against the barium hydroxide solution and found to contain 114.42 millimols HCl per kilogram of solution. Its conductance at 18° agreed closely with the values obtained by Goodwin and Haskell.†

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*In making this test, about 1 gram was dissolved in acetic acid, and a drop of indigo solution and several cubic centimeters of sulphuric acid (1.84 sp. gr.) were added. The blue color remained, whereas when one drop of a 0.1 normal nitric acid was added, the solution was decolorized at once.

†Proc. Am. Acad., **40**, 413 (1904). Phys. Rev., **19**, 386 (1904).

91. DISCUSSION OF ERRORS AND CORRECTIONS.

The errors inherent in the use of the conductivity bomb and the corrections for them are fully discussed in section 10, Part II. A few additional words in regard to the relation of them to the present work will suffice.

In the earlier experiments with sulphuric acid made by Mr. Yogoro Kato the bomb was always charged so as to have only from 1 to 2 c.cm. vapor-space at 218° and no correction for this was applied at any temperature. The air pressure in the bomb was in all cases reduced to 3 or 4 cm. before the first measurement at 18°. The bomb was usually removed and shaken by hand at each temperature before the measurement was made, as the rotating carriage had not at that time been introduced. At 218° with the 0.0005 normal solution a considerable increase of conductance always took place within one or two minutes after the current was passed, but after this time no further change took place even in 15 minutes. The constant values resulting after the passage of the current for 2 minutes or so are those given below in the table. This increase is perhaps due to the throwing out of adsorbed substance from the electrodes. With the 0.002 normal solution the effect was less regular and far less pronounced.

In our own experiments, the air was removed from the bomb only in those extending to 218° or above, since its pressure at the lower temperatures could not have a considerable effect.

The correction for solvent in the vapor space was neglected below 218°, as computation showed that under the prevailing conditions the correction was less than 0.02 per cent even at 156°, where the vapor space measured about 7 c.cm.; nor was this correction applied at 306°, since the vapor space amounted to only 2 to 3 c.cm. and since the specific volume data used are affected by a corresponding error, which at any rate partially eliminates the effect of the vaporization of the solvent on the values of the equivalent conductance, as mentioned in section 10, Part II. At 218° whenever the vapor-space exceeded 2 to 3 c.cm. this correction was made as there described. In the case of hydrochloric acid at 260° the correction for vaporization of the solvent was combined with that for the solute and was computed upon the basis of a direct experiment, which will be now described.

An estimate of the extent to which the solute volatilized was obtained in the cases of nitric acid at 218° and of hydrochloric acid at 260° by comparative experiments in which the bomb was charged with very different quantities of solution so that the vapor-space varied considerably; the difference in conductance was thus found in the case of nitric acid at 218° to correspond to that which would have resulted from the volatilization of the solvent alone. In the case of hydrochloric acid at 260°, the observed change in conductance was only about three-fourths of that which would have resulted from the volatilization of the solvent alone, a fact which indicated some volatilization of the solute.* This was allowed for in all the experiments with hydrochloric acid at 260° by diminishing the calculated correction for solvent-vaporization by one-fourth.

No correction for conductance of the water was applied, except in the case of the neutral salts used in determining the conductance-capacity. Unusually good water was used for the very dilute solutions, the measured specific conductance just before mixing being almost always below 0.5×10^{-6}, and in some cases as low as 0.3×10^{-6}.

The final values of the conductance were corrected for contamination wherever the difference between the initial and final 18° values exceeded 0.25 per cent, by the arbitrary rule that the conductance at the highest temperature of the experiment be increased by two-thirds of the percentage change observed at 18°, and at the next lower temperature by one-fourth of that percentage change. No such correction was applied to the results with hydrochloric acid, since there seemed to be no variation at the higher temperatures corresponding to that at 18°.

The expansion of all the solutions on heating was assumed to be the same as that of pure water and the change in concentration was calculated by dividing the concentration at 4° by the specific volume of pure water at the temperature in question.†

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*The data upon which this conclusion is based are as follows:

Solute.	Concentration at 18°.	Grams of solution in bomb.	Temperature of measurement (t).	Volume of vapor-space at $t°$.	Conductance at $t°$.
HCl	100	95.9	259.8	2	6,057
		56.5	259.8	53	6,158
HNO_3.........	100	84.7	217.8	24	58,070
		102.5	218.2	2	57,870

The concentrations were only approximately those given in the table. The specific volume of the saturated vapor was taken as 85 at 218° and 39 at 260° upon the basis of the estimates referred to in section 34, Part IV.

†For the specific volume the following values were used:

Temp.	Sp. vol.	Temp.	Sp. vol.	Temp.	Sp. vol.
18°......	1.0014	100°......	1.0431	260°......	1.277
25°......	1.0029	128°......	1.0685	306°......	1.433
50°......	1.0119	156°......	1.0980		
75°......	1.0257	218°......	1.1862		

The values at 128° and 156° are derived by graphic interpolation from Hirn's values [Ann. chim. phys. (4), 10, 32 (1867)] after correcting them to the pressures of saturated vapor by means of the compression-coefficient of water, obtained by extrapolating from the data of Pagliani & Vincentini given in the Landolt-Börnstein-Meyerhoffer Tabellen. The values at 218° and 306° are those experimentally determind by Noyes & Coolidge; that at 260° was obtained by graphic interpolation.

92. CONDUCTANCE-CAPACITY OF THE BOMB.

The conductance-capacity of the bomb at 18° (*i. e.* the factor by which the observed conductance must be multiplied to give the specific conductance) was determined with known solutions of sodium and potassium chlorides. The values adopted for the equivalent conductances of these salts are those given by Kohlrausch.*

Table 93 gives the actual conductances in the bomb of the various solutions, diminished by the conductance of the water, as determined from a measurement made just before mixing. Separate fresh solutions were used in each case. The conductances are given in reciprocal ohms, the concentrations in milli-equivalents per liter of solution.

Table 93.—*Conductance-capacity.—Data and final values.*

Date.	Cell No.	Salt.	Concentration at 18°.	Conductance $\times 10^6$.	Conductance-capacity.	
					Separate values.	Final values.
1905						
Aug. 17....	I	KCl..	10.00	*8,195	0.14939	0.14934
Aug. 17....		NaCl.	10.00	*6,829	0.14929	
Aug. 29....	I	KCl..	10.00	*8,201	0.14928	0.14923
Aug. 29...		NaCl.	10.00	6,834	0.14918	
Nov. 20....	II	KCl..	19.963	1,968.4	1.2164	1.2181
Nov. 21....		KCl..	9.982	1,003.1	1.2183	
Nov. 25....		KCl..	99.87	9,184	1.2183	
Nov. 28....		NaCl.	99.88	7,539	1.2192	
1906						
Feb. 3....	II	KCl..	99.98	9,192	1.2186	1.2179
Mar. 7....		NaCl.	10.006	838.1	1.2172	
Mar. 8....		NaCl.	19.986	1,634.6	1.2180	
Mar. 24....	II	NaCl.	49.91	3,916.9	1.2197	1.2193
Mar. 26....		NaCl.	100.00	7,545	1.2197	
Apr. 3....		NaCl.	100.03	7,552	1.2189	
Apr. 9....		KCl..	10.002	1,004.6	1.2190	
July 10....	III	NaCl.	100.00	6,836	1.3461	1.3484
July 24....		KCl..	50.01	4,294.5	1.3485	
July 31....		KCl..	20.015	1,777.8	1.3506	
Sept. 17....	III	KCl..	19.958	1,774.2	1.3495	1.3486
Sept. 28....		KCl..	10.002	908.6	1.3477	

*Mean of two almost completely concordant experiments.

The results dated August, 1905, are those of Mr. Kato. The first of his final values was used in connection with his conductance data obtained up to August 26 inclusive. The second mean value was used with all his later data — those obtained from August 31 to September 16.

In computing the conductance from our measurements made prior to March 20, 1906, the value (1.2181) for the conductance-capacity obtained from the first four determinations made in November, 1905, was used. This will be seen to be substantially identical with that obtained in February and March, 1906. In connection with the data on barium hydroxide (obtained between March 28 and April 4, 1906) the slightly higher value (1.2193) was used, which was derived from the four determinations made during the work on this substance. In connection with the data obtained after July 10, 1906, for which another bomb was used, the last value of the conductance-capacity given in the table was used.

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*Königl. preuss. Akad., 1900, 2, 1002-1008.

The variation of the conductance-capacity with the temperature was computed, as described in section 36, Part IV, from the dimensions of the quartz cup used.*

93. THE CONDUCTIVITY DATA.

Tables 94 to 100 contain the conductivity data for all the solutions. The measurements dated August and September, 1905, were made by Mr. Y. Kato, while all the later ones are our own.

The first column gives the date; the second, the concentration at 4° in milli-equivalents per liter† referred to the equivalent weight of oxygen taken as 8.00 and the weights being reduced to vacuo; the third, the temperature of the measurement expressed on the hydrogen-gas scale; the fourth, the concentration at that temperature calculated as described in section 91; the fifth, the measured conductance in reciprocal ohms, corrections having been applied for the errors in the slide-wire, resistance-coils, and leads, but not for the impurities in the water; the sixth, the equivalent (or molal) conductance calculated from the conductance given in the fifth column, the concentration given in the fourth column, and the value of the conductance-capacity appropriate at that date, as given in section 92, the last being corrected to the temperature of the measurement.

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*This had an effective inside height of 1.45 cm. in Cell II and of 1.40 cm. in Cell III and an inside diameter of 1.40 cm. in Cell II and of 1.37 cm. in Cell III. The percentage corrections applied to the 18° value of the conductance-capacity were the same for the two cells and at the different temperatures were as follows:

50°	75°	100°	128°	156°	218°	260°	306°
—0.06	—0.11	—0.16	—0.21	—0.27	—0.41	—0.52	—0.63

†Except in the cases of phosphoric acid and potassium hydrogen sulphate, where the concentration is expressed in milli-formula-weights per liter at 4°.

Table 94.—*Conductivity data for sulphuric acid up to 218°.*

[Results of Y. Kato.]

Date.	Concentration at 4°.	Temperature t°.	Concentration at t°.	Conductance $\times 10^6$.	Equivalent conductance.
1905					
Aug. 23......	11.748	18.00	11.733	23,660	301.2
		155.9	10.707	34,460	479.9
		217.4	9.913	35,790	537.9
		18.00	11.733	23,920	304.5
Aug. 24......	11.762	18.00	11.747	23,810	302.8
		99.83	11.279	33,040	437.1
		155.9	10.720	34,300	477.2
		217.5	9.924	35,560	533.9
		18.00	11.747	24,020	305.4
Sept. 14......	11.643	18.00	11.627	23,720	304.5
		100.20	11.161	32,970	440.3
		157.6	10.592	34,150	480.3
		217.9	9.818	35,220	533.9
		18.00	11.627	23,720	304.5
Sept. 15......	11.945	18.00	11.927	24,140	301.9
		100.30	11.447	33,730	439.2
		157.9	10.865	35,060	480.7
		218.0	10.070	36,140	534.1
		158.4	10.860	35,220	483.1
		100.30	11.447	33,750	439.5
		18.00	11.927	24,230	303.1
Sept. 16......	11.945	18.00	11.927	24,240	303.8
		100.20	11.447	33,760	440.6
		18.00	11.927	24,240	303.8
Sept. 16......	11.901	18.00	11.886	24,180	303.6
		100.11	11.408	33,650	439.6
		158.0	10.830	34,940	480.6
		217.6	10.039	36,140	535.7
		18.00	11.886	24,180	303.5
Sept. 9......	2.050	18.00	2.047	4,864	354.5
		217.8	1.7287	6,569	565.6
		18.00	2.047	4,866	354.6
Sept. 10......	2.050	18.00	2.047	4,864	354.5
		217.8	1.7287	6,542	563.3
		18.00	2.047	4,866	354.6
Sept. 11......	0.5052	18.00	0.5046	1,265.4	374.1
		100.06	0.4844	2,317	713.0
		156.4	0.4600	2,022	654.6
		217.5	0.4262	1,683.3	587.8
		18.00	0.5046	1,265.4	374.1
Sept. 12......	0.5670	18.00	0.5663	1,409.4	371.5
		99.80	0.5436	2,552	699.9
		156.3	0.5165	2,222	640.7
		217.4	0.4785	1,877.6	584.0
		156.5	0.5165	2,228	642.4
		99.81	0.5436	2,560	702.0
		18.00	0.5663	1,409.9	371.6
Sept. 13......	0.5238	18.00	0.5232	1,307.5	372.9
		99.82	0.5022	2,392	709.9
		156.5	0.4772	2,086	651.1
		217.1	0.4419	1,749.2	589.0
		18.00	0.5232	1,309.9	373.6
Aug. 25......	1.9924	156.3	1.8149	6,590	541.4
		217.5	1.6809	6,337	561.7

TABLE 94.—*Conductivity data for sulphuric acid up to 218°*—Continued.

[Results of Y. Kato.]

Date.	Concentration at 4°.	Temperature at t°.	Concentration at t°.	Conductance $\times 10^6$.	Equivalent conductance.
1905					
Aug. 26......	2.032	156.5	1.8200	6,758	543.6
		217.3	1.7148	6,535	567.7
Aug. 31......	2.047	18.00	2.044	4,838	352.9
		99.82	1.9630	7,545	573.0
Sept. 1......	2.107	18.00	2.104	4,992	353.9
		100.14	2.020	7,751	572.1
		156.0	1.9195	6,954	539.6
		217.5	1.7778	6,710	561.9
		18.00	2.104	5,009	355.1
Sept. 6......	2.091	18.00	2.089	4,965	354.6
		217.2	1.7642	6,667	562.5
		156.0	1.9051	6,932	541.9
		18.00	2.089	4,960	354.3
Sept. 7......	2.075	18.00	2.072	4,868	350.5
		99.95	1.9894	7,651	573.3
		156.2	1.8902	6,904	544.0
		217.7	1.7499	6,766	575.5
		156.4	1.8902	6,920	545.2
		100.05	1.9891	7,675	575.2
		18.00	2.072	4,926	354.7

TABLE 95.—*Additional conductivity data for sulphuric acid.*

[Results of Noyes & Eastman.

Date.	Concentration at 4°.	Temperature t°.	Concentration at t°.	Conductance $\times 10^6$.	Equivalent conductance.
1905					
Dec. 14.......	99.98	18.00	99.84	19,150	233.6
		25.00	99.69	20,590	251.5
		50.00	98.81	24,400	300.6
		75.00	97.48	27,000	337.0
		100.00	95.85	29,130	369.6
		128.0	93.57	31,220	405.6
		156.0	91.06	32,780	437.2
		18.00	99.84	19,140	233.6
1906					
Jan. 5	100.08	18.00	99.94	19,130	233.2
		25.00	99.79	20,580	251.2
1905					
Dec. 12	50.06	18.00	49.99	10,405	253.5
		25.00	49.92	11,196	273.1
		50.00	49.48	13,165	323.9
		75.00	48.81	14,316	356.9
		100.00	48.00	15,214	385.5
		128.0	46.86	16,129	418.4
		155.9	45.60	16,886	449.8
		18.00	49.99	10,399	253.4
1906					
Jan. 3.......	12.503	18.00	12.485	3,092	301.7
		25.00	12.467	3,355	327.7
		50.00	12.356	3,996	393.7
		75.00	12.189	4,241	423.4
		100.00	11.986	4,307	437.0
		128.0	11.701	4,371	454.0
		156.0	11.387	4,475	477.4
		18.00	12.485	3,093	301.7

TABLE 95.—***Additional conductivity data for sulphuric acid***—Continued.

[Results of Noyes & Eastman.]

Date.	Concentration at 4°.	Temperature t°.	Concentration at t°.	Conductance × 10^6.	Equivalent conductance.
1906					
Jan. 1.......	2.0012	18.00	1.9984	580.3	353.7
		25.00	1.9954	640.5	390.9
		50.00	1.9777	815.3	501.9
		75.00	1.9511	902.7	563.0
		100.00	1.9186	906.7	574.8
		128.0	1.8730	859.3	557.7
		156.0	1.8226	813.7	542.3
		18.00	1.9984	580.5	353.8
1905					
Dec. 19......	0.4992	18.00	0.4985	152.0	371.4
		25.00	0.4977	168.8	413.1
		50.00	0.4933	224.1	552.9
		75.00	0.4867	263.0	657.5
		100.00	0.4785	278.9	708.9
		128.0	0.4672	270.2	703.0
		156.0	0.4546	245.2	655.1
		18.00	0.4985	152.7	373.1
Dec. 21......	0.5005	18.00	0.4998	152.7	372.1
		25.00	0.4991	169.8	414.4
		50.00	0.4946	225.2	554.4
		75.00	0.4880	264.3	659.1
		100.00	0.4798	280.5	711.0
		128.0	0.4684	271.7	704.9
		156.0	0.4558	246.7	657.4
		18.00	0.4998	152.9	372.7
1906					
Jan. 10.......	0.1983	18.00	0.1980	61.04	375.5
		25.00	0.1977	68.05	419.2
		50.00	0.1959	91.40	567.8
		75.00	0.1933	110.33	694.5
		100.00	0.1901	122.64	784.6
		128.1	0.1856	124.78	817.4
		156.0	0.1806	115.22	775.1
		18.00	0.1980	61.53	378.5
Jan. 12.......	0.2013	18.00	0.2010	61.73	374.0
		25.00	0.2007	68.87	417.8
		50.00	0.1990	92.56	566.3
		75.00	0.1963	111.91	693.8
		100.00	0.1930	124.35	783.6
		128.1	0.1884	126.87	818.5
		156.0	0.1834	117.29	777.1
		18.00	0.2010	62.80	380.5
Jan. 18.......	0.1989	18.00	0.1986	61.15	375.0
		100.00	0.1907	122.40	780.7
		128.4	0.1861	124.22	811.4
		155.9	0.1812	114.67	768.9
		18.00	0.1986	61.00	374.1
Oct. 20.......	2.647	18.00	2.643	683.5	348.7
		304.3	1.853	882.3	638.1
		18.00	2.643	682.5	348.2
Aug. 26.......	114.67	18.00	114.51	19,501	229.6
		218.0	97.01	34,904	483.3
		303.2	80.62	28,490	473.6
		18.00	114.51	19,387	228.9

TABLE 96.—*Conductivity data for phosphoric acid.*

Date.	Concentration at 4°.	Temperature $t°$.	Concentration at $t°$.	Conductance $\times 10^6$.	Molal conductance.
1906					
Feb. 7.......	0.22663	18.00	0.2263	61.30	329.9
		25.00	0.2260	67.94	366.1
		50.14	0.2240	90.47	491.8
		75.00	0.2210	108.53	597.7
		100.00	0.2173	122.40	685.1
		128.0	0.2121	132.36	758.5
		156.0	0.2064	136.22	801.8
		18.00	0.2263	61.38	330.4
Jan. 22.......	1.9989	18.00	1.9961	463.9	283.1
		25.00	1.9931	510.6	312.0
		50.14	1.9753	651.9	401.8
		75.00	1.9488	745.8	465.7
		100.00	1.9163	792.6	503.0
		128.1	1.8706	795.2	516.7
		156.1	1.8203	753.6	502.9
		18.00	1.9961	463.5	282.9
Jan. 24.......	2.0003	18.00	1.9974	464.5	283.3
		25.00	1.9945	511.1	312.1
		50.14	1.9767	652.8	402.0
		75.00	1.9502	747.0	466.1
		100.00	1.9176	793.7	503.3
		128.0	1.8721	796.5	517.2
		156.1	1.8216	754.9	503.4
		18.00	1.9974	464.2	283.1
Jan. 26.......	12.507	18.00	12.489	1,962	191.3
		25.00	12.471	2,133	208.3
		50.14	12.360	2,592	255.3
		75.00	12.194	2,814	280.8
Jan. 29.......	12.501	18.00	12.483	1,960.4	191.3
		100.00	11.984	2,839.6	288.2
		128.0	11.699	2,699.7	280.5
		156.0	11.385	2,436.5	260.0
		75.00	12.187	2,814.3	281.0
		18.00	12.483	1,960.3	191.3
		25.00	12.464	2,131.7	208.3
		50.14	12.353	2,590.0	255.3
Jan. 30.......	50.016	18.00	49.94	5,034	122.8
		25.00	49.87	5,435	132.7
		50.14	49.43	6,441	158.6
		75.00	48.76	6,823	170.3
		100.00	47.95	6,727	170.6
		128.0	46.81	6,251	162.3
		156.0	45.55	5,533	147.6
		18.00	49.94	5,032	122.7
Feb. 1.......	100.00	18.00	99.86	7,918	96.6
		25.00	99.71	8,524	104.1
		50.14	98.83	10,004	123.3
		75.00	97.49	10,509	131.2
		100.00	95.87	10,292	130.6
		128.0	93.60	9,501	123.4
		156.0	91.07	8,377	111.7
		18.00	99.86	7,911	96.5

TABLE 97.—*Conductivity data for nitric acid.*

Date.	Concentration at 4°.	Temperature $t°$.	Concentration at $t°$.	Conductance × 10^6.	Equivalent conductance.
1906					
Feb. 20.......	0.5010	18.00	0.5003	153.66	374.1
		25.00	0.5000	171.06	417.0
		50.14	0.4951	229.65	564.7
		75.00	0.4884	279.88	697.2
		100.00	0.4803	321.85	815.0
		127.8	0.4690	358.88	930.1
		155.8	0.4564	386.33	1,028.3
		18.00	0.5003	153.49	373.7
Feb. 24.......	0.4975	18.00	0.4968	152.51	373.9
		100.00	0.4769	319.68	815.2
		156.00	0.4531	383.73	1,028.8
		18.00	0.4968	152.60	374.1
Feb. 26.......	1.9688	18.00	1.9661	599.2	371.2
		25.00	1.9631	666.8	413.7
		50.00	1.9457	893.3	558.9
		75.00	1.9196	1,090.0	691.0
		100.00	1.8874	1,252.2	806.8
		128.0	1.8426	1,394.9	920.1
		156.0	1.7931	1,496.6	1,013.9
		18.00	1.9661	598.4	370.8
Feb. 28.......	12.498	18.00	12.481	3,728	363.9
		25.00	12.462	4,144	405.0
		50.00	12.351	5,542	546.3
		75.00	12.185	6,747	673.7
		100.00	11.981	7,719	783.5
		128.0	11.697	8,555	889.0
		156.1	11.382	9,132	974.7
		18.00	12.481	3,720	363.1
Mar. 2......	50.02	18.00	49.95	14,505	353.7
		25.00	49.88	16,108	393.3
		50.00	49.43	21,464	528.6
		75.00	48.77	26,028	649.4
		100.00	47.95	29,621	751.2
		128.0	46.81	32,637	847.4
		156.0	45.56	34,554	921.4
		18.00	49.95	14,491	353.4
Mar. 5......	100.12	18.00	99.98	28,430	346.4
		25.00	99.83	31,560	385.0
		50.00	98.94	41,930	515.9
		75.00	97.61	50,740	632.5
		100.00	95.98	57,600	729.9
		128.00	93.70	63,210	820.0
		156.1	91.18	66,530	885.9
		18.00	99.98	28,420	346.3
Oct. 18.......	2.277	18.00	2.274	625.0	370.7
		218.3	1.918	1,661.6	1,163
		18.00	2.274	620.6	368.1
Oct. 11.......	2.879	18.00	2.875	790.8	370.9
		303.9	2.021	1,733.7	1,150
		18.00	2.875	781.2	366.4
Aug. 25......	100.12	18.00	99.98	25,654	346.0
		217.8	84.72	58,072	920.5
		303.6	70.29	26,233	500.1
		18.00	99.98	25,361	342.0
Nov. 12......	100.12	18.00	99.98	25,629	345.7
		218.2	84.38	57,870	921.0
		18.00	99.98	25,629	345.7

TABLE 98.—*Conductivity data for barium hydroxide.*

Date.	Concentration at 4°.	Temperature t°.	Concentration at t°.	Conductance × 10^6.	Equivalent conductance.
1906 Mar. 28......	0.5011	18.00	0.5004	90.1	219.5
		25.00	0.4996	102.9	251.0
		50.00	0.4952	150.1	369.3
		75.00	0.4886	197.5	492.4
		100.00	0.4804	240.6	609.7
		128.0	0.4689	280.0	727
		156.0	0.4563	301.9	804
		18.00	0.5004	56.2	136.9
Apr. 4.......	2.000	18.00	1.997	352.4	215.2
		50.00	1.976	580.1	357.7
		100.00	1.917	921.6	585.2
		156.0	1.821	1,187.9	793.1
		18.00	1.997	323.0	197.2
Apr. 5.......	2.003	18.00	2.000	353.9	215.8
		50.00	1.979	583.1	359.0
		100.00	1.920	927.0	587.8
		18.00	2.000	351.0	214.0
Apr. 6.......	12.516	18.00	12.499	2,106	205.4
		25.00	12.480	2,393	232.8
		50.00	12.369	3,432	338.1
		75.00	12.203	4,438	443.1
		100.00	11.999	5,333	541.1
		156.0	11.400	6,609	705.1
		100.00	11.999	5,260	533.7
		18.00	12.499	2,069	201.8
Apr. 2.......	49.99	18.00	49.92	7,822	191.1
		25.00	49.85	8,794	215.1
		50.00	49.40	12,508	308.5
		75.00	48.74	15,982	399.4
		100.00	47.92	18,893	480.1
		128.0	46.79	21,214	551.7
		156.0	45.53	22,316	596.0
		18.00	49.92	7,730	188.8
Mar. 21......	99.98	18.00	99.84	14,750	180.1
		25.00	99.69	16,700	204.3
		50.00	98.80	23,630	291.5
		75.00	97.48	29,950	374.3
		100.00	95.85	35,080	445.5
		128.0	93.57	38,910	506.0
		156.0	91.06	40,290	538.1
		18.00	99.84	14,680	179.3

TABLE 99.—*Conductivity data for potassium hydrogen sulphate.*

Date.	Concentration at 4°.	Temperature $t°$.	Concentration at $t°$.	Conductance $\times 10^6$.	Molal conductance.
1906					
Jan. 8.......	100.19	18.00	100.05	21,660	263.7
		25.00	99.90	23,230	283.2
		50.00	99.01	26,820	329.7
		75.00	97.68	28,570	355.9
		100.00	96.05	29,810	377.4
		128.0	93.77	31,350	406.4
		156.1	91.24	33,100	440.7
		18.00	100.05	21,660	263.7
Jan. 16.......	1.994	18.00	1.991	744.5	455.5
		25.00	1.988	827.0	506.6
		50.00	1.970	1,072.0	662.3
		75.00	1.944	1,210.4	757.6
		100.00	1.911	1,240.8	789.5
		128.0	1.866	1,198.9	780.9
		156.0	1.816	1,137.8	761.2
		18.00	1.991	743.0	454.5
*July 10......	50.04	18.00	49.97	10,971	295.5
		25.00	49.90	11,804	318.4
		50.00	49.45	13,795	375.3
		75.00	48.79	14,689	404.9
		100.00	47.97	15,181	425.3
		128.0	46.83	15,728	451.1
		156.0	45.57	16,426	483.8
		18.00	49.97	10,969	295.5

*The conductance-capacity here used was that of Cell III as determined July 10, namely, 1.3461 at 18°.

TABLE 100.—*Conductivity data for hydrochloric acid.*

Date.	Concentration at 4°.	Temperature $t°$.	Concentration at $t°$.	Conductance $\times 10^6$.	Equivalent conductance.
1906					
July 18.......	2.870	18.00	2.866	796.1	374.5
		259.6	2.259	2,232	1,326
		305.9	2.003	2,001	1,338
		18.00	2.866	793.5	373.3
July 19.......	14.327	18.00	14.307	3,899	367.4
		259.6	11.274	10,227	1,216.8
		306.5	9.985	8,650	1,160.8
		18.00	14.307	3,797	357.8
July 21.......	14.323	18.00	14.303	3,893	367.0
		259.1	11.284	10,223	1,215.2
		303.6	10.059	8,778	1,169.4
		18.00	14.303	3,852	363.1
July 22.......	114.60	18.00	114.44	29,586	348.6
July 25.......	114.60	18.00	114.44	29,551	348.1
		260.3	90.04	69,396	1,034.0
		303.3	80.56	52,604	875.1
		18.00	114.44	29,300	345.2
Sept. 19......	2.873	18.00	2.869	797.2	374.8
		304.0	2.015	2,015	1,340
		18.00	2.869	795.9	374.2
Sept. 25......	14.281	18.00	14.261	3,882	367.1
		304.1	10.016	8,728	1,168
		18.00	14.261	3,873	366.2
Sept. 26......	114.42	304.0	80.27	53,240	872.2
		18.00	114.26	......	348.8

94. SUMMARY OF THE VALUES OF THE EQUIVALENT CONDUCTANCE.

Tables 101 to 107 contain a summary of the values of the equivalent conductance given in the preceding tables. Kato's values (and a few other values) have been corrected to round temperatures by means of temperature-coefficients obtained from a plot of them. In no case, except at 218° and above, did the correction exceed 0.2 per cent of the whole. In the few experiments where the difference between the initial and final values at 18° exceeds 0.25 per cent, the values at the highest temperatures have been corrected for contamination as described in section 91. When such a correction has been applied it has been indicated in the tables by affixing the letter c to the value in question.

Table 101.—*Equivalent conductance of sulphuric acid.*

[Results of Y. Kato.]

Date.	Concentration at 4°.	18°		100°		156°		218°.
		Initial.	Final.	Initial.	Final.	Initial.	Final.	
1905								
Sept. 11..	0.5052	374.1	374.1	713.0	......	655.4	......	588.0
Sept. 12..	0.5670	371.5	371.6	700.0	702.1	641.3	643.4	584.2
Sept. 13..	0.5238	372.9	373.6	710.0	......	652.1	......	589.3
Mean .	0.532	372.8	373.1	707.7	......	649.6	......	587.2
Aug. 25..	1.992	......	......	......	......	541.5	......	562.1
Aug. 26..	2.032	......	......	......	......	543.7	......	568.2
Aug. 31..	2.047	352.9	......	573.0	......	......	......	......
Sept. 1..	2.107	353.9	355.1	572.1	......	539.6	......	561.0^{c}
Sept. 6..	2.091	354.6	354.3	......	......	......	541.9	563.1
Sept. 7..	2.075	350.5	354.7	573.3	575.2	544.1	545.3	571.1^{c}
Sept. 9..	2.050	354.5	354.6	......	......	......	......	565.7
Sept. 10..	2.050	354.5	354.6	......	......	......	......	563.4
Mean .	2.070	353.5	......	......	......	......	......	......
	2.076	......	......	572.8	......	......	......	......
	2.052	......	......	......	......	542.2	......	......
	2.057	......	......	......	......	......	......	564.9
Aug. 23..	11.748	301.2	304.5	......	......	480.0	......	534.6^{c}
Aug. 24..	11.762	302.8	305.4	437.2	......	477.3	......	530.8^{c}
Sept. 14..	11.643	304.5	304.5	440.2	......	478.8	......	534.0
Sept. 15..	11.945	301.9	303.1	439.0	439.3	478.9	480.8	532.7^{c}
Sept. 16..	11.945	303.8	303.8	440.5	......	......	......	......
Sept. 16..	11.901	303.6	303.5	439.5	......	478.7	......	536.1
Mean .	11.824	302.9	304.2	......	......	......	......	......
	11.839	......	......	439.3	......	......	......	......
	11.820	......	......	......	......	478.7	......	533.5

TABLE 102.—*Equivalent conductance of sulphuric acid.*

[Results of Noyes & Eastman.]

Date.	Concentration at 4°.	18°		25°.	50°.	75°.	100°.	128°.	156°.
		Initial.	Final.						
1905									
Jan. 10..	0.1983	375.5	378.5	419,2	567.8	694.5	784.6	815.9^c	769.0^c
Jan. 12..	0.2013	374.0	380.5	417.8	566.3	693.8	783.6	814.9^c	771.0^c
Jan. 18..	*0.1989	375.0	374.1	......	......	......	780.7	812.1^c	769.7^c
Means .	0.1995	374.9	376.8	......	......	......	782.4	813.7	769.8
	0.1998	......	......	418.5	567.0	694.1	......	......	......
Dec. 19..	0.4992	371.4	373.1	413.1	552.9	657.5	708.9	702.2^c	653.1^c
Dec. 21..	0.5005	372.1	372.7	414.4	554.4	659.1	711.0	704.9	657.4
Mean .	0.4999	371.8	372.9	413.7	553.6	658.3	709.9	703.6	655.2
1906									
Jan. 1..	2.001	353.7	353.8	390.9	501.9	563.0	574.8	557.7	542.3
Jan. 3..	12.50	301.7	301.7	327.7	393.7	423.4	437.0	454.0	477.4
1905									
Dec. 12..	50.06	253.5	253.4	273.1	323.9	356.9	385.5	418.4	450.0
Dec. 14..	99.98	233.6	233.6	251.5	300.6	337.0	369.6	405.6	437.2
1906									
Jan. 5..	100.08	233.2	......	251.2	......	......	......	......	......
Means .	99.98	......	......	......	300.6	337.0	369.6	405.6	437.2
	100.03	233.4	......	251.3	......	......	......	......	......
					218°	306°			
Oct. 20..	2.647	348.7	348.2	......	......	639	......	......	......
Aug. 26..	114.67	229.6	228.9	......	484^c	474^c	......	......	......

*This experiment was given double weight in computing the mean, on account of the smaller contamination.

TABLE 103.—*Molal conductance of phosphoric acid.*

Date.	Concentration at 4°.	18°		25°.	50°.	75°.	100°.	128°.	156°.
		Initial.	Final.						
1906									
Feb. 7..	0.2266	329.9	330.4	366.1	491.1	597.7	685.1	758.5	801.8
Jan. 22..	1.999	283.1	282.9	312.0	401.3	465.7	503.0	516.7	503.0
Jan. 24..	2.000	283.3	283.1	312.1	401.6	466.1	503.3	517.2	503.5
Mean .	2.000	283.2	283.0	312.0	401.4	465.9	503.2	517.0	503.2
Jan. 26..	12.51	191.3	......	208.3	255.1	280.8	......	......	......
Jan. 29..	12.50	191.3	191.3	208.3	255.1	281.0	288.2	280.5	260.0
Mean .	12.50	191.3	......	208.3	255.1	280.9	288.2	280.5	260.0
Jan. 30..	50.02	122.8	122.7	132.7	158.5	170.3	170.6	162.3	147.6
Feb. 1..	100.00	96.6	96.5	104.1	123.2	131.2	130.6	123.4	111.7

TABLE 104.—*Equivalent conductance of nitric acid.*

Date.	Concentration at 4°.	18°		25°.	50°.	75°.	100°.	128°.	156°.
		Initial.	Final.						
1906									
Feb. 20.	0.5010	374.1	373.7	417.0	563.9	697.2	815.0	930.9	1,029.0
Feb. 24.	0.4975	373.9	374.1	......	......	......	815.2	......	1,028.8
Mean ..	0.4992	374.0	373.9	......	......	......	815.1	......	1,028.9
	0.5010	......	......	417.0	563.9	697.2	......	930.9	......
Feb. 26.	1.969	371.2	370.8	413.7	558.9	691.0	806.8	920.1	1,013.9
Feb. 28.	12.50	363.9	363.1	405.0	546.3	673.7	783.5	889.0	974.4
Mar. 2.	50.02	353.7	353.4	393.3	528.6	649.4	751.2	847.4	921.4
Mar. 5.	100.12	346.4	346.3	385.0	515.9	632.5	729.9	820.0	885.7

Date.	Concentration at 4°.	18°		218°.	306°.
		Initial.	Final.		
1906					
Oct. 18.............	2.277	370.7	368.1	1,168	......
Oct. 11.............	2.879	370.9	366.4	......	1,155
Aug. 25.............	100.12	346.0	342.0	923^{c}	482^{c}
Nov. 12.............	100.12	345.7	345.7	921	......
Mean	100.12	345.9	......	922	......

TABLE 105.—*Equivalent conductance of barium hydroxide.*

Date.	Concentration at 4°.	18°		25°.	50°.	75°.	100°.	128°.	156°.
		Initial.	Final.						
1906									
Mar. 28.	0.5011	219.5	136.9	251.0	*369.3	*492.4	*610	*800^{c}	* 1,000^{c}
Apr. 4.	2.000	215.2	197.2	......	357.7	......	589^{c}	......	840^{c}
Apr. 5†	2.003	215.8	214.0	......	359.0	......	591^{c}	......	......
Mean .	2.002	215.5	......	......	358.6	......	591	......	840
Apr. 6.	12.52	205.4	201.8	232.8	338.1	443.1	‡541.1	......	713^{c}
Apr. 2.	49.99	191.1	188.8	215.1	308.5	399.4	480.1	553.4^{c}	600.8c
Mar. 21.	99.98	180.1	179.3	204.3	291.5	374.3	445.5	506.6^{c}	539.7c

*Very rough approximation, owing to great contamination.

†Double weight, on account of smaller contamination.

‡A final value at 100°, after going to 156°, was 533.7.

§This same correction for contamination was applied to this value as to the one below it, *i. e.*, two thirds of the percentage change at 18° in the second experiment.

TABLE 106.—*Molal conductance of potassium hydrogen sulphate.*

Date.	Concentration at 4°.	18°		25°.	50°.	75°.	100°.	128°.	156°.
		Initial.	Final.						
1906									
Jan. 16..	1.994	455.5	454.5	506.6	662.3	757.6	789.5	780.9	761.2
July 10..	50.04	295.5	295.5	318.4	375.3	404.9	425.3	451.1	483.7
Jan. 8..	100.19	263.7	263.7	283.2	329.7	355.9	377.4	406.4	440.7

Table 107.—*Equivalent conductance of hydrochloric acid.*

Date.	Concentration at 4°.	18°		260°.	306°.
		Initial.	Final.		
1906					
July 18...	2.870	374.5	373.3	1,326	1,338
Sept. 19...	2.873	374.8	374.2	......	1,336
Mean ...	2.872	374.6	......	1,326	1,337
July 19...	14.33	367.4	357.8	1,217	1,162
July 21...	14.32	367.0	363.1	1,216	1,162
Sept. 25...	14.28	367.1	366.2	......	1,162
Mean ...	14.31	367.2	......	1,216	1,162
July 22...	114.60	348.6	......	......	......
July 25...	114.60	348.1	345.2	1,035	862
Sept. 26...	114.42	......	348.8	......	862
Mean ...	114.5	348.4	......	1,035	862

The degree of concordance of the results of the experiments carried only to 156° may be first considered. An examination of the preceding tables shows that for sulphuric, phosphoric, and nitric acids and potassium hydrogen sulphate in solutions 2 milli-normal and stronger, the agreement between the initial and final values at 18°, and between duplicate experiments is in general better than 0.2 per cent, the greatest difference being 0.22 per cent. The same is also true of the 0.2 milli-molal phosphoric acid and of the 0.5 milli-normal nitric acids. In the 0.2 and 0.5 milli-normal sulphuric acid solutions, however, the final values at 18° are somewhat larger than the initial, averaging 0.5 and 0.3 per cent respectively. The independent experiments at these two concentrations agreed within about the same limits, the greatest average deviation from the mean being 0.22 per cent. Kato's values (table 101) show about the same differences as our own between the intial and final 18° values, except in three experiments which show an increase of about 1 per cent. A comparison of his individual experiments with one another can hardly be made owing to large differences in concentration, but his final means compared after reducing to round concentrations agree with our own within 0.2 per cent, except at 100° in the 0.5 and 2.0 milli-normal where the differences reach 0.4 per cent. The divergence between the initial and final 18° values for barium hydroxide increases rapidly with the dilution, amounting to 0.4 per cent at 100 milli-normal, 1.2 per cent at 50 milli-normal, 8 per cent at 2 milli-normal, and 38 per cent at 0.5 milli-normal, in cases where the solution had been heated to 156°. These large changes in the dilute solutions make, of course, the observed values of the conductance at the higher temperatures very inaccurate; but the error has been doubtless reduced to a relatively small amount (except for the 0.5 milli-normal solution) by the correction applied for the contamination as described in section 91.

In the experiments extended to 218°, 260°, and 306° the agreement was not so good, owing to greater contamination. In the first experiments with hydrochloric acid, made in July, 1906, the final values at 18° differed from the initial values by one to three per cent (except in the most dilute solution). This seems to have been due to the presence of gold and platinum dissolved from the lining; for the strongest solution had a light yellow color after the heating, and a small precipitate of gold and a brown coloration was obtained on adding stannous chloride. To diminish this solvent action, the solutions in the later experiments made in September were boiled at about 60° under reduced pressure just after they were introduced into the bomb; and it was then found that the initial and final values at 18° agreed within 0.3 per cent. The fact that the two sets of experiments gave concordant results at 306° shows that the presence of the gold or platinum had no influence at that temperature, probably owing to the hydrolysis of their salts. Differences of about one per cent were observed in some of the experiments with nitric and sulphuric acid, but these solutions did not contain gold or platinum in appreciable quantity.

In the course of the experiments with the 2 milli-normal nitric acid, the remarkable phenomenon was observed in four or five cases that the conductance rapidly decreased during the heating above 200°, owing evidently to decomposition of the acid. Thus, in one case after heating to 306° it was found that the final conductance at 18° was only five per cent of the initial value. This decomposition was apparently started by minute quantities of impurities accidentally introduced into the bomb; for it was found possible to prevent it by making up the solution with exceptionally pure water and taking special precautions against contamination.* This behavior is entirely analogous to that of silver nitrate as observed by Noyes and Melcher and described in section 39, Part IV.

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*The nitric acid seems to decompose into nitrogen (or nitrous oxide), oxygen, and water; for tests for nitrite and for ammonia made by the processes used in water analysis on a 2 milli-normal solution which had been heated to 218° and had greatly decreased in conductance showed that the quantities of these substances present were less than 0.1 per cent of the nitric acid originally in the solution.

95. FINAL VALUES OF THE EQUIVALENT CONDUCTANCE AT ROUND CONCENTRATIONS.

The mean values of the equivalent or molal conductance given in tables 101 to 107 have been reduced to round concentrations by the help of coefficients derived from curves obtained by plotting Λ against some function of the concentration (C), or of the product ΛC. The error introduced in reducing in this way to round concentrations probably exceeds 0.1 or 0.2 per cent only for those values, inclosed within parentheses in the table below, which it was necessary to correct for a fairly large difference in concentration.

The equivalent conductances at zero concentration (Λ_0) have been obtained in the cases of nitric acid, phosphoric acid, and barium hydroxide at temperatures up to 156° by extrapolation upon plots of $1/\Lambda$ against $(\Lambda C)^{n-1}$, as described in section 17, Part II (except that those for barium hydroxide at 75° and 128° were obtained, by interpolation, from a plot of the other Λ_0 values against the temperature). The Λ_0-value for hydrochloric acid at 306° was obtained in the same way; but to get that at 260° the value of the exponent n was assumed to be 1.50, since the data were not sufficient to determine this with accuracy. The Λ_0-values for nitric acid at 218° and 306° were assumed to be 97 per cent of those for hydrochloric acid at these temperatures, just as they are at 100° and 156°. Owing to the contamination in the more dilute solution, the Λ_0-values for barium hydroxide at the higher temperatures are only rough approximations; and owing to the long extrapolation, those for hydrochloric and nitric acids at 260° and 306° may well be in error by two to three per cent. The Λ_0-values for sulphuric acid at 18°, 100°, 156°, 218° and 306° were obtained by the equation

$$\Lambda_{0\mathrm{H_2SO_4}} = \Lambda_{0\mathrm{HCl}} + \Lambda_{0\mathrm{K_2SO_4}} - \Lambda_{0\mathrm{KCl}}$$

using the values for hydrochloric acid, potassium sulphate, and potassium chloride given in table 36, (§ 54, Part V), table 22, (§ 41, Part IV), and table 9 (§ 16, Part II), respectively. Those at the intermediate temperatures were obtained from the others by graphic interpolation.

The final values so obtained are all given in tables 108 and 109. The temperatures are those of the hydrogen-gas scale. The concentration is expressed in milli-equivalents (or milli-formula-weights) of solute per liter of solution at the temperature of the measurement, the atomic weight of oxygen being taken as 16.00 and the weights of substances being corrected for air buoyancy; milli-formula-weights per liter are given for phosphoric acid and potassium hydrogen sulphate, milli-equivalents per liter for all the other substances. The equivalent or molal conductance is expressed in reciprocal ohms; the molal conductance is given in the case of phosphoric acid and potassium hydrogen sulphate, the equivalent conductance in all other cases.

TABLE 108.—*Final values of the equivalent or molal conductance up to 218°.*

Substance.	Concentration.	18°.	25°.	50°.	75°.	100°.	128°.	156°.	218°.
HNO_3	0.0	377	421	570	706	826	945	1,047	(1,230)
	0.5	374.0	417.0	563.9	697.1	814.8	930	1,028	......
	2.0	371.2	413.7	558.8	689.7	806.2	919	1,012	1,166
	10.0	(365)	(406)	(548)	(676)	(786)	(893)	(978)	......
	12.5	363.9	405.0	546.2	673.4	782.7	887	972	......
	50.0	353.7	393.3	528.4	648.9	750.1	845	917	......
	80.0	(349)	(388)	(521)	(637)	(735)	(827)	(893)	926
	100.0	346.4	385.0	515.7	631.8	728.4	817	880	......
H_2SO_4	0.0	383	(429)	(591)	(746)	891	(1,041)	1,176	1,505
	0.2	374.9	418.5	566.9	693.6	779.6	807	759	......
	0.5	371.8	413.7	553.4	657.0	706.3	696	644	586
	2.0	353.9	390.8	501.3	560.8	571.0	551	536	563
	10.0	(309)	(337)	(406)	(435)	(446)	(460)	(481)	533
	12.5	301.3	327.5	393.1	421.9	434.9	452	475	529
	50.0	253.5	273.0	323.4	356.0	384.3	417	448	(502)
	80.0	(240)	(258)	(306)	(342)	(373)	(408)	(440)	(488)
	100.0	233.3	251.2	300.3	336.4	368.8	404	435	(483)
H_3PO_4	0.0	338	376	510	631	730	839	930	......
	0.2	330.8	367.2	493.0	600.3	688.5	762.1	804.7	......
	2.0	283.1	311.9	400.7	463.6	498.2	507.6	489.0	......
	10.0	(203)	(222)	(273)	(300)	(308)	(298)	(274)	......
	12.5	191.2	208.1	254.1	278.5	283.9	273.6	250.5	......
	50.0	122.7	132.6	157.8	168.6	167.8	158.0	142.0	......
	80.0	(104)	(112.4)	(133)	(141)	(141)	(134)	(118)	......
	100.0	96.5	104.0	122.7	129.9	128.4	120.2	107.7	......
$Ba(OH)_2$	0.0	222	256	389	(520)	645	(760)	847	......
	0.5	219	251	......	......	......	......	......	......
	2.0	215	.....	359	......	591	......	......	......
	10.0	(207)	(235)	(342)	(449)	(548)	(664)	(722)	......
	12.5	205.4	232.8	338	442	539	......	707	......
	50.0	191.1	215.1	308	399	478	549	593	......
	80.0	(184)	(208)	(296)	(382)	(454)	(516)	(551)	......
	100.0	180.1	204.2	291	373	443	503	531	......
$KHSO_4$	2.0	455.3	506.3	661.0	754.1	784.0	773	754	......
	10.0	(379)	(417)	(508)	(558)	(580)	(600)	(611)	......
	50.0	295.5	318.3	374.4	402.8	422.1	446	477	......
	80.0	(273)	(294)	(343)	(369)	(389)	(415)	(448)	......
	100.0	263.7	283.1	329.1	354.4	374.6	(402)	435	......

TABLE 109.—*Final values of the equivalent conductance at 260° and 306°.*

Substance.	Concentration.	260°.	306°.
HCl	0.0	1,380	1,424
	2.0	1,332	1,337
	10.0	1,226	1,162
	80.0	1,046	862
HNO_3..........	0.0	......	(1,380)
	2.0	......	1,156
	70.0	......	482
	80.0	......	(454)
H_2SO_4..........	0.0	......	(2,030)
	2.0	......	637
	80.0	......	474

The values given in table 109 for sulphuric acid are the means of those obtained by Mr. Kato and ourselves in the case of the 2 and 12.5 milli-normal solutions. The values derived by each were as follows:

Concentration.	18°		100°		156°	
	Kato.	N. & E.	Kato.	N. & E.	Kato.	N. & E.
0.5	373.2	371.8	709.0	706.3	645	644
2.0	354.1	353.7	572.2	569.8	536	535
12.5	301.0	301.7	434.8	435.0	475.4	475.3

We regard our values for the very dilute 0.5 milli-normal solution as more reliable because of the fact that our bomb was rotated, thus removing any contamination from the immediate neighborhood of the electrodes.

Table 110 contains a comparative summary of the results at 18° of previous investigations and of our own. From all the earlier values the conductance of the water has been subtracted, while in the case of our values, this has not been done; but the conductance of the water used (0.3 to 0.5 $\times$ 10^{-6} at 18°) amounted to only about 0.2 per cent of that of the 0.5 milli-normal acid solutions. Interpolated values are inclosed within parentheses.

TABLE 110.—*Comparison of the conductance values at* 18° *with those of other investigators.*

Concentration.	Sulphuric acid.			Phosphoric acid.		Nitric acid.		
	Kohlrausch.*	Whetham.†	Noyes & Eastman.	Foster.‡	Noyes & Eastman.	Goodwin & Haskell.§	Kohlrausch.*	Noyes & Eastman.
0.2	......	(379)	374.9	312	330.8	......	......	......
0.5	(368)	(376)	371.8	(312)	(320)	373.9	......	373.9
2.0	351	(350)	353.7	279	283.1	371.4	374	371.2
12.5	......	......	......	(189)	191.2	......	......	......
50.0	253	......	253.5	(122.9)	122.7	......	357	353.7
100.0	225	......	233.3	(96.7)	96.5	......	350	346.4

*Kohlrausch & Holborn, Leitvermögen der Elektrolyte, p. 160.

†Interpolated from a plot of the values given by Whetham in Z. phys. Chem., 55, 205 (1906). These values are dependent on Kohlrausch's at 0.02-0.03 normal.

‡Phys. Rev. 8, 269 (1899). Interpolated from a plot.

§Proc. Am. Acad., 40, 413 (1904); Phys. Rev., 19, 386 (1904).

Our values for sulphuric acid agree fairly well with those of Kohlrausch and of Whetham, except for the concentration 100 milli-normal, where our value is 3.6 per cent greater than that of Kohlrausch. On account of this discrepancy, a check measurement was made (on May 14, 1906) at this concentration in a U-shaped glass vessel; and the value 233.6 was obtained for the equivalent conductance, which differs by less than 0.2 per cent from the determination made in the bomb. The values for the stronger solutions of phosphoric acid agree very well with Foster's; but our values for the dilute solutions are considerably greater than his, the difference being 5.5 per cent at 0.2 milli-molal. This divergence is doubtless largely due to the fact that Foster subtracted the conductance of the water, which in this case amounted to 3.6 per cent of the whole conductance. The values for nitric acid in the dilute solutions are in excellent agreement with those of Goodwin and Haskell, who used a special method to eliminate the effect of impurities in the water. For the stronger solutions, our values exceed Kohlrausch's by about 1 per cent; but here, as for sulphuric acid, our value was checked (on May 11, 1906) by an independent measurement of a 100 milli-normal solution in a U-shaped vessel, whereby the value 346.8 (instead of 346.4) was obtained.

96. CHANGE OF THE EQUIVALENT CONDUCTANCE WITH THE CONCENTRATION AND THE TEMPERATURE.

As in the previous researches in this series we have determined what value of *n* must be used in the equation $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$ to make it conform to the results. The values of the exponent so obtained are given in table 111.

Table 111.—*Values of the exponent n in the function* $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$

Substance.	18°.	25°	50°.	75°.	100°.	128°.	156°.
HNO_3........	1.43	1.43	1.43	1.43	1.45	1.45	1.45
H_3PO_4.......	1.9	....	....	....	1.8	....	1.8
$Ba(OH)_2$..	1.55	1.45	1.40	....	1.45	....	1.45

The values of the exponent at 260° and 306° for hydrochloric acid were found to be 1.35 and 1.60, respectively, while Noyes and Cooper's values (see table 39, Part V) at the lower temperatures range from 1.38 to 1.47. For sulphuric acid at 18° (up to 50 milli-normal) the exponent has the value of 1.5; it was not determined at the higher temperatures because the ionization-relations are there complicated by the presence in large quantity of the intermediate HSO_4^- ion. It will be seen from these results that the conductance of nitric acid and hydrochloric acid changes with the concentration according to the same law as does that of the neutral salts; and that the same is true of the tri-ionic base barium hydroxide and of the tri-ionic acid sulphuric acid at 18°. The insignificant variation of the exponent with the temperature in the case of all these substances is also worthy of notice. It is of interest, too, to note that the exponent for phosphoric acid, which is only moderately ionized, is intermediate between that found for the largely ionized substances and that required by the mass-action law.

The change of the Λ_0-values with the temperature deserves consideration only in the cases of nitric acid, phosphoric acid, hydrochloric acid and barium hydroxide; for only for these substances were they directly derived. Table 112 contains the ratios of these Λ_0-values to those previously given for potassium chloride and for some other substances.

TABLE 112.—*Ratio of the Λ_0-values to those for potassium chloride and other substances.*

	18°.	100°.	156°.
HNO_3 : KCl	2.90	1.99	1.67
HNO_3 : HCl	0.99	0.97	0.97
HNO_3 : $Ba(OH)_2$	1.70	1.28	1.24
H_3PO_4 : KCl	2.60	1.76	1.49
H_3PO_4 : HCl	0.89	0.86	0.86
$Ba(OH)_2$: KCl	1.71	1.56	1.36
$Ba(OH)_2$: $Ba(NO_3)_2$	1.90	1.67	1.53

The ratio HCl:KCl at 306° was found to be 1.27; its value at lower temperatures was found by Noyes and Cooper to be as follows: 2.91 at 18°, 2.05 at 100°, 1.73 at 156°, and 1.53 at 218°. It will be observed that the ratio of the values for hydrochloric and nitric acids is not far from unity at all temperatures, showing that the chloride and nitrate ions always move at nearly the same rate. The values of the other ratios show that the velocities of the hydrogen and hydroxide ions approach those of each other and of the neutral-salt ions as the temperature rises.

Table 113 contains the values of the mean temperature-coefficients of the conductance at zero concentration ($\Delta\Lambda_0/\Delta t$) for the substances included in this investigation. It will be seen that all these values steadily decrease, showing that the conductance-temperature curve is concave toward the temperature axis and that it has no points of inflexion, as is the case with neutral salts.

TABLE 113.—*Mean temperature-coefficients of the conductance at zero concentration.*

Substance.	Temperature interval.				
	18°–50°.	50°–100°.	100°–156°.	156°–218°.	218°–306°.
HNO_3	6.03	5.12	3.95	......	......
H_2SO_4	6.50	6.00	5.09	......	......
H_3PO_4	5.22	4.50	3.57	......	......
BaO_2H_2	5.22	5.12	3.58	......	......
HCl	......	......	4.20	2.90	1.81

With reference to the effect of temperature on the conductance values at the higher concentrations, attention may be called to the fact that maximum values are reached in the cases of all the acids investigated, namely, near 75° with 0.1 molal and near 128° with 0.002 molal phosphoric acid, between 156° and 218° with 0.08 normal nitric acid, and between 218° and 260° with 0.08 normal hydrochloric acid. Sulphuric acid shows a very different variation of the conductance with the temperature at different concentrations. This is best seen by reference to figure 18, on which the values for 0.08 normal hydrochloric and nitric acids are also plotted. The most striking feature of this plot is that the conductance values for the most concentrated and the most dilute sulphuric acid at first diverge rapidly with rising temperature (up to about 100°), then approach each other (most closely at 218°), and finally again diverge. This behavior can be satisfactorily accounted for by assuming that the dissociation of this acid takes place in two stages according to the reactions:

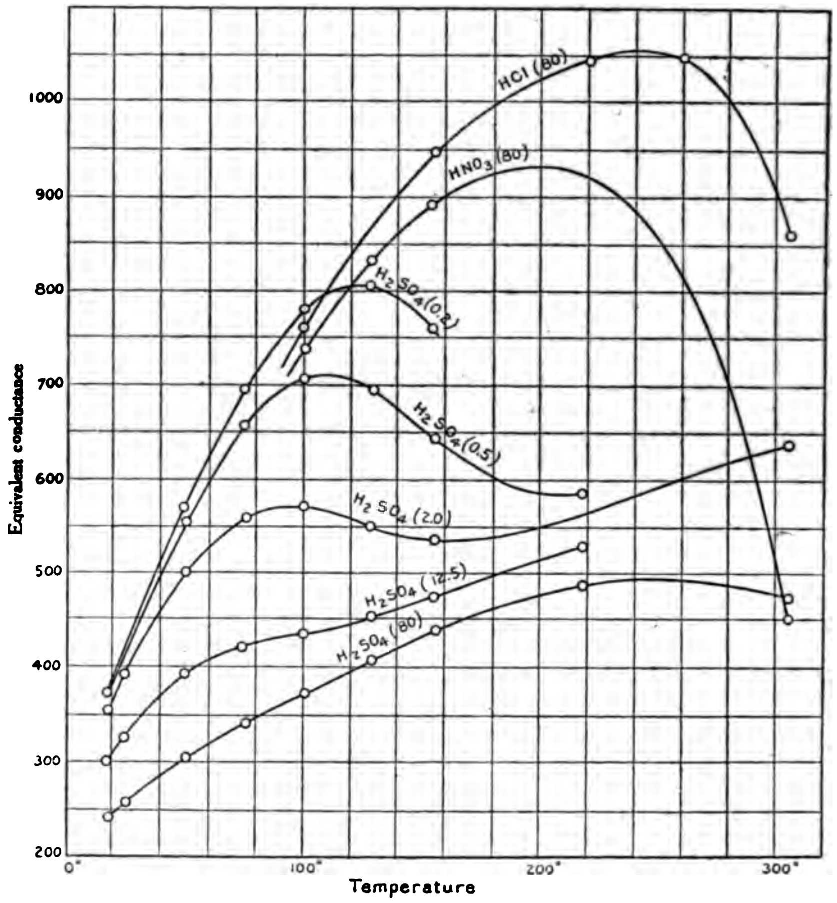

Fig. 18.

$$H_2SO_4 = H^+ + HSO_4^- \text{ and } HSO_4^- = H^+ + SO_4^{=}$$

and that the extent to which these two reactions occur is very different at the different temperatures. This matter will be discussed in the following section.

97. IONIZATION OF THE SUBSTANCES AND ITS CHANGE WITH THE CONCENTRATION AND THE TEMPERATURE.

Tables 114 and 115 contain the values of the ratio 100 Λ/Λ_0 for the substances for which the equivalent or molal conductances are given in tables 108 and 109. This ratio doubtless represents approximately the percentage ionization in the cases of nitric and phosphoric acids, and almost certainly also in the case of barium hydroxide; for the second hydrogen of phosphoric acid has been shown by the work of Mr. G. A. Abbott[*] to be less than 0.05 per cent ionized at 18° at even 0.001 molal concentration; and the equivalent conductance of barium hydroxide behaves at all temperatures so entirely like that of neutral uni-univalent and unibivalent salts that it is hardly probable that any considerable quantity of an intermediate ion like $BaOH^+$ exists. In the case of sulphuric acid, two sets of ratios separated by a dash are given in table 114; the first one is 100 times the ratio of the equivalent conductance (Λ) of the acid at the concentration in question to the sum of the equivalent conductances of the hydrogen and sulphate ions ($\Lambda_H + \Lambda_{SO_4}$), for which sum the values were given in tables 109 and 110; the second one is 100 times the ratio of the equivalent conductance Λ to the sum of the equivalent conductances of the hydrogen and the hydrosulphate ion ($\Lambda_H + \Lambda_{HSO_4}$), for which sum values equal to the Λ_0 values for acetic acid were taken, it being assumed that the latter ion has the same equivalent conductance as the $C_2H_3O_2^-$ ion, whose molecule consists of nearly the same number of atoms. These two ratios represent the limits between which must lie the percentage of the total hydrogen of the acid which exists in the state of hydrogen-ion in the solution; for if the acid dissociated wholly into $2H^+ + SO_4^=$, this percentage would have the first value, and, if wholly into H^+ and HSO_4^- the second value.[†] The value of the percentage ionization would evidently be the same as the first value if the acid dissociated only in the first way, and twice the second value if it dissociated only in the second way.

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[*] Reference is here made to a research executed in this laboratory, but not yet published.

[†] This will be evident from the following considerations. The specific conductance L of the solution is given in the two cases by the expressions

$$\mathrm{L} = C_H \Lambda_H + 2C_{SO_4}\Lambda_{SO_4} \text{ and } \mathrm{L} = C_H\Lambda_H + C_{HSO_4}\Lambda_{HSO_4}$$

where the large *C's* represent molal concentrations; or since $C_H = 2C_{SO_4}$ in the first case and $C_H = C_{HSO_4}$ in the second, also by:

$$\mathrm{L} = C_H(\Lambda_H + \Lambda_{SO_4}) \text{ and } \mathrm{L} = C_H(\Lambda_H + \Lambda_{HSO_4});$$

from which by substituting for L its value $\mathrm{c}\Lambda$ where c is the equivalent concentration of the acid, we obtain:

$$\frac{C_H}{\mathrm{c}} = \frac{\Lambda}{\Lambda_H + \Lambda_{SO_4}} \text{ and } \frac{C_H}{\mathrm{c}} = \frac{\Lambda}{\Lambda_H + \Lambda_{HSO_4}}$$

TABLE 114.—*Conductance-ratio 100 Λ/Λ_0 and approximate percentage ionization up to 218°.*

Substance.	Concentration.*	18°.	25°.	50°.	75°.	100°.	128°.	156°.	218°.
HNO_3.....	0.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100
	0.5	99.1	99.0	98.9	98.7	98.6	98.4	98.2	......
	2.0	98.4	98.2	98.0	97.7	97.6	97.2	96.7	95
	10.0	96.8	96.4	96.1	95.8	95.2	94.5	93.4	......
	12.5	96.4	96.2	95.8	95.4	94.8	93.9	92.8	......
	50.0	93.7	93.4	92.7	91.9	90.8	89.4	87.6	......
	80.0	92.6	92.2	91.4	90.2	89.0	87.5	85.3	75
	100.0	91.8	91.4	90.5	89.5	88.2	86.5	84.0	......
H_3PO_4....	0.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	......
	0.2	98.0	97.5	96.5	95.0	94.5	91.0	86.5	......
	2.0	84.0	83.0	78.5	73.5	68.5	60.5	52.5	......
	10.0	60.0	59.0	53.5	47.5	42.0	35.5	29.4	......
	12.5	56.5	55.5	50.0	44.0	39.0	32.5	27.0	......
	50.0	36.5	35.0	31.0	26.5	23.0	19.0	15.5	......
	80.0	31.0	30.0	26.0	22.5	19.5	16.0	12.5	......
	100.0	28.5	27.5	24.0	20.5	17.5	14.5	11.5	......
H_2SO_4....	0.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100
	0.2	98–108	98–108	96–107	93–105	87–104	78–91	65–77	......
	0.5	97–107	97–106	94–104	88–100	79–91	67–79	55–66	39–50
	2.0	92–102	91–101	85–95	75–85	64–74	53–62	46–55	37–48
	10.0	81–89	79–87	69–77	58–66	50–58	44–52	41–49	35–46
	12.5	79–87	76–84	66–74	57–64	49–56	43–51	40–48	35–45
	50.0	66–73	64–70	55–61	48–54	43–50	40–47	38–46	33–43
	80.0	63–69	60–66	52–58	46–52	42–48	39–46	37–45	32–42
	100.0	61–67	59–65	51–57	45–51	41–48	39–46	37–44	32–41
$Ba(OH)_2$..	0.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	......
	0.5	98	98	......	......	......	......	......	......
	2.0	97	(96)	92	......	91	......	......	......
	10.0	93	92	88	86	85	87	85	......
	12.5	92	91	87	85	83	......	83	......
	50.0	86	84	79	77	74	72	70	......
	80.0	83	81	76	73	70	68	65	......
	100.0	81	80	75	72	68	66	63	......

*Milli-equivalents per liter in the cases of nitric and sulphuric acids and of barium hydroxide; milli-formula-weights per liter in the case of phosphoric acid.

TABLE 115.—*Conductance-ratio 100 Λ/Λ_0 and approximate percentage ionization at 260° and 306°.*

Substance.	Concentration.	260°.	306°.
HNO_3.....	0.0	....	100
	2.0	....	84
	80.0	....	33
HCl.......	0.0	100	100
	2.0	96	94
	10.0	89	82
	80.0	76	60
H_2SO_4....	0.0	....	100
	2.0	....	31–50
	80.0	....	23–37

It has already been shown that the equivalent conductances of nitric acid and of barium hydroxide up to 156° and that of hydrochloric acid up to 306° change with the concentration according to the same exponential law as does that of neutral salts, the value of the exponent n in the equation $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$, being in all cases approximately 1.5. It follows therefore that the same is true of the ionization (γ) of these substances, to which the corresponding equation $C(1-\gamma) = K(C\gamma)^n$ with $n = 1.5$, approximately, applies.

The change of ionization with the temperature of nitric acid up to 156° and of hydrochloric acid even up to 306° is also about the same magnitude as that of neutral salts of the same ionic type, as may be seen best by comparing the values at 80 milli-normal in tables 114 and 115 and table 41, Part V, with those in table 28 (Part IV). Thus at 18° the ionization of potassium and sodium chlorides is 86.5 per cent, that of hydrochloric and nitric acids 93 per cent, while at 156° the corresponding values are 80.5 per cent for the two salts and 86 per cent for the two acids. At 306° the ionization of the salts is 63 per cent and that of hydrochloric acid 60 per cent. The ionization of nitric acid, however, at 218° and above decreases much more rapidly than hydrochloric acid, and has fallen to 33 per cent at 306°. This marked difference in the behavior of the two acids at the high temperatures is well shown by the conductance plot in fig. 18. The ionization of barium hydroxide decreases a little more rapidly than the average ionization of the two salts, barium nitrate and potassium sulphate; thus at 0.08 normal that of the base is 83 per cent at 18° and 65 per cent at 156°, while that of the salts is 72 per cent at 18° and 60 per cent at 156°.

It was shown in the last section that the exponent in the functional relation between equivalent conductance and concentration in the case of phosphoric acid has values (1.8 to 1.9) which approach much more nearly to the value (2.0) required by the mass-action law, but do not entirely conform to it, even at the higher temperatures where the ionization is comparatively small. To show better what the order of magnitude of this deviation is, and to furnish a better basis of comparison of the ionization-tendency of this acid with that of other weaker acids, we have summarized in table 116 its ionization-constants calculated by the usual formula $K = C\gamma^2/(1-\gamma)$, the concentration C being here expressed in formula-weights per liter, and the constants being multiplied by 10^6.

TABLE 116.—*Ionisation-constants for phosphoric acid.*

Concentration.	Ionization-constants × 10^6.						
	18°.	25°.	50°.	75°.	100°.	128°.	156°.
0.0125	9,200	8,700	6,300	4,300	3,100	1,960	1,250
0.050	10,400	9,400	7,000	4,800	3,400	2,230	1,420
0.100	11,400	10,400	7,600	5,300	3,700	2,460	1,490

The great effect of temperature in reducing the ionization of this acid will be apparent from an inspection of these constants or of the ionization values themselves given in table 114.

The values given for sulphuric acid in tables 114 and 115 show the percentage of the total hydrogen which exists as hydrogen-ion under the two limiting assumptions that the acid dissociates on the one hand only into hydrogen-ion and sulphate-ion and on the other only into hydrogen-ion and hydrosulphate-ion (HSO_4^-). It will be seen that the two limits do not differ greatly from each other, except at the highest temperatures, and therefore that the uncertainty as to the hydrogen-ion concentration, which is really the most important datum relating to the acid, is not very large. It is evident that this hydrogen-ion concentration decreases rapidly with rising temperature; for example, at 0.08 normal from about 66 per cent at 18° to about 45 per cent at 100° and about 30 per cent at 306°, if the mean values be taken.

By this hydrogen-ion concentration, however, not much light is thrown on the extent to which the two stages in the dissociation take place. It might seem that additional information in regard to this could be derived from the transference determinations made at 11°, 23°, and 96° by Bein* and between 8° and 32° by Tower.† But calculation shows that the transference numbers of the cathion calculated under the two limiting assumptions of dissociation only into hydrogen-ion and sulphate-ion and of dissociation only into hydrogen-ion and hydrosulphate-ion (HSO_4^-) do not differ from each other by much more than the possible experimental error or than the error arising from the uncertainty in the values to be assumed for the equivalent conductance of the separate ions.‡ The conclusion previously drawn by one of us§ from Tower's transference data that sulphuric acid at 18° up to 0.2 normal does not contain an important quantity of hydrosulphate-ion is therefore not justified in consideration of the effect of the possible errors.

Further light is thrown on the ionization relations of sulphuric acid through a consideration of those of potassium hydrogen sulphate. Conclusions in regard to the hydrogen-ion concentration in solutions of this salt may be drawn from its molal conductance (Λ), provided we make certain approximate assumptions. For, designating by γ_1, γ_2, and γ_3 the

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*Z. phys. Chem., **27**, 52 (1898). †J. Am. Chem. Soc., **26**, 10 (1904).

‡Thus at 18° assuming $\Lambda_{H} = 315$, $\Lambda_{SO_4} = 68$, and $\Lambda_{HSO_4} = 35$, the two transference numbers for the cathion are 0.822 and 0.800, while, if as concluded by Noyes & Kato (see section 116, Part XI) $\Lambda_{H} = 335$ (for a 0.05 normal solution), the two transference numbers become 0.831 and 0.811. Tower found 0.823 and Bein 0.813 at 18°. The value of Λ_{HSO_4} is also very uncertain.

§A. A. Noyes, Z. phys. Chem., **53**, 251 (1905).

fraction of the salt which dissociates according to the three reactions

$$KHSO_4 = K^+ + HSO_4^-,$$
$$KHSO_4 = K^+ + H^+ + SO_4^=, \text{ and}$$
$$2KHSO_4 = 2K^+ + SO_4^= + H_2SO_4$$

respectively,* it is evident that

$$\Lambda = \gamma_1(\Lambda_K + \Lambda_{HSO_4}) + \gamma_2(\Lambda_K + \Lambda_H + 2\Lambda_{SO_4}) + \gamma_3(\Lambda_K + \Lambda_{SO_4})$$

or, putting $\gamma = \gamma_1 + \gamma_2 + \gamma_3$, that

$$\Lambda = \gamma(\Lambda_K + \Lambda_{HSO_4}) + \gamma_2(\Lambda_H + 2\Lambda_{SO_4} - \Lambda_{HSO_4}) + \gamma_3(\Lambda_{SO_4} - \Lambda_{HSO_4}).$$

Now the two limiting values of γ_3 are zero and $\gamma - \gamma_2$ (when $\gamma_1 = 0$), whence it follows that

$$\gamma_2 < \frac{\Lambda - \gamma(\Lambda_K + \Lambda_{HSO_4})}{(\Lambda_H + \Lambda_{SO_4}) + (\Lambda_{SO_4} - \Lambda_{HSO_4})} \text{ and } \gamma_2 > \frac{\Lambda - \gamma(\Lambda_K + \Lambda_{SO_4})}{\Lambda_H + \Lambda_{SO_4}}$$

Limiting values of γ_2, the fraction dissociated into hydrogen-ion, can be calculated in this way from the data presented in this monograph with the help of the assumptions that the un-ionized fraction $(1 - \gamma)$ of the salt has the same value as in the case of other salts of the uni-univalent type at the same concentration and temperature, and that the equivalent conductance of the hydrosulphate-ion is the same as that of the acetate ion at the same temperature. Table 117 contains the results of these calculations† for four concentrations at 18°, 100°, and 156°.

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*The dissociation according to the reactions $2KHSO_4 = K_2SO_4 + H^+ + HSO_4^-$ and $2KHSO_4 = K_2SO_4 + 2H^+ + SO_4^=$ is neglected in this preliminary calculation; but the K_2SO_4 formed must be small in most cases owing to the small concentration of sulphate-ion.

†The data used are as follows:

	18°.		100°.		156°.	
$\Lambda_K + \Lambda_{SO_4}$	133		455		715	
$\Lambda_K + \Lambda_{HSO_4}$	99		337		520	
$\Lambda_{SO_4} - \Lambda_{HSO_4}$	34		118		195	
$\Lambda_H + \Lambda_{SO_4}$	382		891		1175	
$\Lambda_H + \Lambda_{HSO_4}$	348		778		980	
C	2	10	2	10	2	10
Λ	455	379	784	580	754	611
γ	0.97	0.94	0.96	0.92	0.95	0.91
C	50	100	50	100	50	100
Λ	296	264	422	375	477	435
γ	0.88	0.85	0.85	0.81	0.83	0.79

The values of Λ are copied from table 108. Those of γ are the mean ionizations for potassium and sodium chlorides as given in table 12, Part II.

TABLE 117.—*Preliminary values of the percentage ratio* ($100\gamma_2$) *of hydrogen-ion concentration to total hydrogen concentration in solutions of potassium hydrogen sulphate.*

Concentration.	18°.	100°.	156°.
2	85–86	39–46	6–19
10	67–69	18–27	0–10
50	47–50	4–13	0– 3
100	40–43	1–10	0– 2

These preliminary values are given here, because they are essential to the fuller discussion of the ionization-relations of sulphuric acid and its acid salt. More accurate values of the hydrogen-ion concentration in solutions of this salt are derived below and will be found in table 119.

It is seen from these results that at 18° the potassium hydrogen sulphate is in 0.002 molal solution almost completely dissociated into hydrogen-ion and sulphate-ion; but that in 0.1 molal solution this dissociation has taken place only to an extent of 42 per cent, the rest of the salt existing to an extent of 15 per cent as un-ionized $KHSO_4$ and to an extent of 43 per cent either as HSO_4^- or as $H_2SO_4 + SO_4^{=}$. At 100° the hydrogen-ion concentration has become very much less at all three concentrations, and at 156° in the 0.1 molal solution it is scarcely appreciable. This justifies the conclusion that sulphuric acid itself at 156° and above is at moderate dilutions dissociated only into hydrogen-ion and hydrosulphate-ion; for the dissociation of the latter ion would of course be much less in the solution of the acid than of its acid salt, owing to the presence in the former of the hydrogen-ion coming from the dissociation of the first equivalent of hydrogen. Since under these conditions sulphuric acid dissociates as a monobasic acid, it is of interest to compare its ionization with that of hydrochloric acid at the same molal concentration, say at 0.04 molal. The ionization of sulphuric acid may be obtained by doubling the second values given in tables 114 and 115, that of hydrochloric acid by interpolation between the values given for other concentrations in table 115 and in table 41, section 56, Part V. The ionization values for the 0.04 molal acids are as follows:

	100°.	156°.	218°.	306°.
HCl........	92	90	86	68
$H.HSO_4$.....	*96	90	84	74

This shows that the two acids have at these temperatures not far from the same ionization-tendency (with reference in the case of sulphuric acid to the primary dissociation, that is, that of the first equivalent of hydrogen); and it may reasonably be assumed that the same is true at 18° and the intermediate temperatures.

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*This value is doubtless a little too high because of slight secondary ionization.

With the help of this principle, the secondary ionization of the sulphuric acid — that is, the ratio of the sulphate-ion concentration to the total sulphuric acid concentration — can be calculated for the more dilute solutions and for the lower temperatures by means of the relation

$$\frac{C_{SO_4}}{C} = \frac{C_H}{C} + \frac{C_{H_2SO_4}}{C} - 1$$

where C represents the total molal concentration of the sulphuric acid, and the other symbols, the molal concentrations of the separate substances as indicated by the subscripts. This relation follows at once from a combination of the equations, $C = C_{H_2SO_4} + C_{HSO_4} + C_{SO_4}$ and $C_H = C_{HSO_4} + 2\,C_{SO_4}$, the latter of which is an expression of the fact that hydrogen-ion is produced by the two chemical reactions $H_2SO_4 = H^+ + HSO_4^-$ and $H_2SO_4 = 2\,H^+ + SO_4^=$.

We have first made a preliminary calculation of the ratio C_{SO_4}/C by the above expression by using for C_H/C twice the mean of the pairs of values given in table 114 of the ratio of the hydrogen-ion concentration to the total hydrogen-concentration, and by taking for $C_{H_2SO_4}/C$ the values of the corresponding ratio for hydrochloric acid as derived from ionization data given in table 41, Part V. We have then on the basis of this result, which shows the approximate proportion of sulphate-ion and hydrosulphate-ion in the solution, interpolated a more correct value of the hydrogen-ion concentration between the two limiting values given in tables 114 and 115, which, it will be remembered, were obtained under the two limiting assumptions that the acid dissociates only into H^+ and $SO_4^=$ and that it dissociates only into H^+ and HSO_4^-.* Then new, final values of the concentrations of the sulphate-ion and hydrosulphate-ion were obtained by repeating the calculation.

The values derived through these considerations are all brought together in table 118. It will be understood, of course, that they are only rough approximations. The concentrations are milli-formula-weights per liter, in accordance with the formula represented by the subscripts. The symbol C represents the total concentration of the acid in milli-formula-weights of H_2SO_4 per liter. But in calculating the values of the ionization-constant given in the last column, the concentrations are all expressed in formula-weights (not milli-formula-weights) per liter.

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*Designating these two limiting values (multiplied by 2) by C'_H/C and C''_H/C, respectively, it can be readily shown by formulating the exact conductance equations that we get for the true value of C_H/C:

$$\frac{C_H}{C} = \frac{C'_H}{C} + \frac{C_{HSO_4}}{C}\left(\frac{C''_H - C'_H}{C''_H}\right) = \frac{C''_H}{C} - \frac{2C_{SO_4}}{C}\left(\frac{C''_H - C'_H}{C'}\right).$$

TABLE 118.—*The ionization-relations of sulphuric acid.*

Temperature.	Concentration.	$\frac{100\ C_H}{C}$	$\frac{100\ C_{H_2SO_4}}{C}$	$\frac{100\ C_{HSO_4}}{C}$	$\frac{100\ C_{SO_4}}{C}$	$\frac{10^6\ C_H \cdot C_{SO_4}}{C_{HSO_4}}$
18	1	185	1	13	86	(12,000)
	5	165	2	31	67	18,000
	25	137	5	53	42	27,000
	50	127	6	61	33	34,000
100	1	136	2	60	38	860
	5	111	4	80	16	1,100
	25	98	7	88	5	1,390
	50	95	9	87	4	(2,200)
156	1	106	3	88	9	110
	5	97	5	93	2	100
	25	89	9	93	−2	......
	50	88	12	88	0	......
218	1	96	3	98	−1	......
	5	..	6	..	..	......
	40	85	14	87	(−1)	......
306	1	97	5	(93)	(2)*	......
	40	70	32	(66)	(2)*	......

*These values probably arise from experimental error.

We may next consider the ionization-relations of the potassium hydrogen sulphate. It follows from the principle that the primary ionization of the sulphuric acid is the same as that of hydrochloric acid that the concentration of the un-ionized sulphuric acid is always so small in the solutions of the potassium hydrogen sulphate that the calculation of the hydrogen-ion concentration made under the assumption that the former concentration (or γ_8) is zero is substantially correct, and therefore that the second or larger numbers given in table 117 are more nearly the true values for the hydrogen-ion concentration. In order to get fairly accurate values for the sulphate-ion and hydrosulphate-ion concentrations in solutions of the salt, it is, however, desirable to form an estimate of the concentration of the un-ionized sulphuric acid (H_2SO_4) and the un-ionized potassium sulphate (K_2SO_4). As the latter was entirely disregarded in the previous calculation, a more accurate value of the hydrogen-ion concentration will also be thereby obtained.

In deriving these final values we have proceeded as follows. We make the preliminary assumption that $C_{SO_4} = C_H$ (taking for C_H/C the larger of the two values given in table 117), and that $C_{HSO_4} = C\gamma - C_{SO_4}$. Applying then the mass-action principle* that in a mixture of two substances with a common ion the un-ionized fraction of each is the same as

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*That this principle is also applicable to salts of these types, even though the change of their ionization with the concentration does not conform to the mass-action law, has been shown by Noyes (Z. phys. chem., **52**, 634, 1905).

if it were alone present at such a concentration that its ions are at a concentration equal to that of the common ion in the mixture, we determine the ratios $\frac{C_{K_2SO_4}}{C_{K_2SO_4}+C_{SO_4}}$ and $\frac{C_{KHSO_4}}{C_{KHSO_4}+C_{HSO_4}}$ by reference to the ionization values given in table 27, Part IV, and in table 12, Part II, for potassium sulphate and for potassium chloride, respectively, at the same concentration of the total potassium.* In a similar way we obtained the ratio $C_{H_2SO_4}/(C_{H_2SO_4}+C_{HSO_4})$ by determining from the data given in table 118 the value of this ratio for sulphuric acid when present alone in a solution in which the hydrogen-ion concentration is the same as that in the solution of the acid-salt under consideration. From these ratios and the preliminary values of C_{SO_4} and C_{HSO_4}, final values of $C_{K_2SO_4}$, C_{KHSO_4}, and $C_{H_2SO_4}$ are calculated. From these C_K is also obtained by means of the equation $C_K + C_{KHSO_4} + 2\,C_{K_2SO_4} = C$, where C is the molal concentration of the potassium hydrogen sulphate. It follows now from the two equations,

$$C_H + C_{HSO_4} + C_{KHSO_4} + 2\,C_{H_2SO_4} = C$$

$$\text{and } C_{SO_4} + C_{HSO_4} + C_{KHSO_4} + C_{H_2SO_4} + C_{K_2SO_4} = C,$$

$$\text{that } C_{SO_4} = C_H + C_{H_2SO_4} - C_{K_2SO_4}$$

$$\text{and } C_{HSO_4} = C - C_H - 2\,C_{H_2SO_4} - C_{KHSO_4}.$$

We have then calculated final values of C_H by the following equation, which expresses the molal conductance Λ of the salt in terms of the equivalent conductances and molal concentrations of the separate ions, $C\Lambda = C_K\Lambda_K + C_H\Lambda_H + C_{HSO_4}\Lambda_{HSO_4} + 2\,C_{SO_4}\Lambda_{SO_4}$. In this equation all the quantities except C_H are known or can be expressed in terms of C_H and known quantities with the help of the two preceding equations. The equation then becomes

$$\frac{C_H}{C}(\Lambda_H + \Lambda_{SO_4} + \Lambda_{SO_4} - \Lambda_{HSO_4}) = \Lambda - \frac{C_K}{C}(\Lambda_K + \Lambda_{HSO_4}) + \frac{2(C_{K_2SO_4} - C_{H_2SO_4})}{C}(\Lambda_{SO_4} - \Lambda_{HSO_4})$$

From the values of C_H/C so obtained we have finally calculated C_{SO_4}/C

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*Whether one considers the ionization at the same concentration of the potassium-ion or of the total potassium makes no substantial difference.

and C_{HSO_4}/C by the two equations just referred to.* All the final values are brought together in table 119. The symbols represent the concentrations in milli-formula-weights per liter of the substance indicated by the subscripts, except that in calculating the ionization-constants formula-weights instead of milli-formula-weights were used.

TABLE 119.—*The ionization-relations of potassium hydrogen sulphate.*

Temperature.	Concentration (C)	$\frac{100\,C_K}{C}$	$\frac{100\,C_H}{C}$	$\frac{100\,C_{SO_4}}{C}$	$\frac{100\,C_{HSO_4}}{C}$	$\frac{100\,C_{H_2SO_4}}{C}$	$\frac{100\,C_{K_2SO_4}}{C}$	$\frac{100\,C_{KHSO_4}}{C}$	$\frac{10^6\,C_H \cdot C_{SO_4}}{C_{HSO_4}}$
18	2	90	89	84	11	0	5	0	13,600
	10	81	74	65	25	0	9	1	19,000
	50	70	57	46	35	2	13	4	37,000
	100	63	51	38	38	2	15	7	51,000
100	2	86	50	45	46	1	6	2	980
	10	81	31	26	60	2	7	5	1,340
	50	76	17	14	65	3	6	12	1,830
	100	71	14	10	65	3	7	15	2,160
156	2	88	22	19	72	1	4	4	116
	10	86	12	11	76	2	3	8	174
	50	79	5	4	76	2	3	15	......
	100	75	3	3	72	3	3	19	......

An examination of the values of 100 C_{SO_4}/C in tables 118 and 119 shows that the secondary ionization of the sulphuric acid into hydrogen-ion and sulphate-ion at 18° is fairly complete in 0.002 molal solution and that it is large, though far from complete, in 0.05 molal solution; also that with rising temperature this secondary ionization decreases very fast and becomes scarcely appreciable in the stronger solutions at 156°. Although the values of the ionization-constant given in the last column of the tables vary considerably with the concentration — probably owing mainly to the fact that the ionization is so large and partly, especially at the higher temperatures, to experimental errors — yet the effect of temperature upon

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*In these calculations the following data, obtained from the three tables mentioned just above, were used, in addition to those given in the foot-note to table 117 and that table itself:

Temperature.	Concentration (C).	$\frac{100\,C_{KHSO_4}}{C_{HSO_4}}$.	$\frac{100\,C_{K_2SO_4}}{C_{SO_4}}$.	$\frac{100\,C_{H_2SO_4}}{C_{HSO_4}}$.
18	2	3	6	1
	10	6	15	2
	50	14	30	4
	100	18	39	5
100	2	4	13	1
	10	9	25	2
	50	18	41	4
	100	23	61	5
156	2	5	18	2
	10	10	33	3
	50	21	61	3
	100	27	78	4

them is seen to be extremely large; thus at 0.01 molal concentration the constants are about 18 times as great at 18° as at 100°, and 8 times as great at 100° as at 156°.

The fair agreement at the same concentration and temperature of the constants derived from the conductance data for the acid and from those for the acid salt is also noteworthy; for, in consideration of the different kinds of data and of approximate assumptions involved in the computations, this agreement is evidence of the substantial correctness of the results. In this connection it may also be mentioned that our value (31 per cent) for the hydrogen-ion concentration at 100° in a 0.01 molal solution of potassium hydrogen sulphate agrees almost completely with the value (31.5 per cent) found by Trevor[*] for 0.01 molal sodium hydrogen sulphate from a study of its catalytic effect on the inversion of cane sugar.

The heat of ionization of the hydrosulphate-ion can be estimated in two ways: first, from the change of its ionization-constant with the temperature; and second, from existing heat-of-neutralization measurements combined with our ionization values. Partly for the sake of a knowledge of this quantity itself, and partly because an agreement of the values obtained in the two ways would furnish further evidence of the correctness of the ionization values derived above, it seems worth while to describe these calculations and their results.

By integrating the well-known equation[†] derived from the Second Law of Energetics $\frac{d \log K}{dT} = \frac{\Delta U}{RT^2}$ under the assumption that the internal-energy-increase ΔU attending the reaction is a linear function of the temperature as expressed by the equation $\Delta U = \Delta U_0 + aRT$, we obtain the expression:

$$\log \frac{K_2}{K_1} - a \log \frac{T_2}{T_1} = \frac{\Delta U_0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

By substituting in this the values of the ionization-constant K in one case at 100° and 18° and in another case at 156° and 100°[‡] two simultaneous equations were obtained, from which the values of ΔU_0 and α in calories were calculated and found to be 14,170 and −32.5, respectively. From these constants the value of ΔU is found to be −4,750 calories at 18° and −10,070 calories at 100°. These values represent the heat absorbed when the reaction $HSO_4^- = H^+ + SO_4^=$ takes place in the direction from left to right, the negative sign showing of course that heat is in reality evolved.

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[*] Z. phys. Chem., **10**, 342 (1892).

[†] The application of this equation to a substance, like hydrosulphate-ion, whose dissociation does not follow the mass-action law, can hardly give accurate results; but it seems probable that it will yield a rough approximation to the truth, at any rate in the case of a substance having an ionization intermediate between that of salts and that of weak acids, provided the values of K at the two temperatures be taken at the same concentration.

[‡] As values of K at 100° and 18° we have used the means of the values derived from the data for the 0.005 molal acid and for the 0.01 molal acid-salt; namely, 1220×10^{-6} at 100°, and 18500×10^{-6} at 18°; and as values of K at 156° and 100° we have used the corresponding means at 0.001 and 0.002 molal; namely, 115×10^{-6} at 156°, and 920×10^{-6} at 100°. We have taken for R the round value 2 calories per degree.

To compute this same energy-change by the second method mentioned above, we used the thermochemical data of Thomsen* which show that, when at 18° one mol of NaOH dissolved in 100 mols of water is added to one mol of $NaHSO_4$ dissolved in 200 mols or 3600 grams of water, 16,630 calories are evolved. Subtracting from this the mean value, 13,770 calories, found by Wörmann† at 18° for the heat of neutralization of nitric and hydrochloric acids by sodium and potassium hydroxides, we get 2860 calories, which represents approximately the heat evolved by the ionization of that quantity of HSO_4 which exists as ion and as un-ionized $KHSO_4$ or H_2SO_4 in the acid sulphate solution employed, it being assumed that the small heat-effect attending the dissociation of the un-ionized $KHSO_4$ or H_2SO_4 into HSO_4^- and K^+ or H^+ is nearly compensated by the heat-effect attending the formation out of its ions of the new quantity of un-ionized K_2SO_4 resulting after the neutralization. Now, the acid sulphate solution under consideration was about 0.28 molal; and our results recorded in table 119 show that a 0.05 molal solution contains 41 per cent and a 0.1 molal solution 47 per cent of the salt in the three forms just mentioned. From these last data we may conclude that the corresponding percentage in a 0.28 molal solution would almost certainly lie somewhere between 54 and 60. Assuming the mean value of 57 per cent, we obtain for the heat absorbed when one mol of hydrosulphate-ion dissociates at 18° −2,860/0.57 or −5,020 calories, a value which agrees with that (−4,750 calories) derived from the ionization-constants fully as closely as could be expected, considering the character of the data involved.

The ionization-constant of the hydrosulphate-ion is still so large at 156° (115×10^{-6}) that neutral sulphates of strong bases would not be appreciably hydrolyzed at this temperature, even at a concentration of 0.002 normal. To determine whether this is still the case at the higher temperature of 218° has an important bearing on the interpretation of the conductivity results obtained with potassium sulphate by Noyes and Melcher (section 44, Part IV). Assuming that the heat of ionization of hydrosulphate-ion continues to change with the temperature according to the linear equation derived from the ionization data at 18°, 100°, and

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*Thermochemische Untersuchungen, 1, 100 - 102 (1882).

†Drude's Ann. Phys., **18**, 793 (1905).

156°, its ionization-constant can be calculated by the integrated equation given above. Such a calculation leads to a value of 12×10^{-6} at 218°; and from this and the ionization-constant of water determined by Sosnan (section 86, Part VII) the hydrolysis (C_{HSO_4}/C_{SO_4}) of potassium sulphate at 0.002 normal at 218° is found to be 0.04 per cent. Though these values are to be regarded only as rough estimates, yet they show that the hydrolysis of potassium sulphate is insignificant under these conditions. Finally it may be mentioned that this value of the ionization-constant would signify that in a 0.002 normal sulphuric acid solution at 218° the secondary ionization (C_{SO_4}/C_{HSO_4}) amounts to only 1.3 per cent.

98. SUMMARY.

In this article have been presented the results of conductance measurements with dilute solutions of nitric, sulphuric, and phosphoric acids, potassium hydrogen sulphate, and barium hydroxide at 25° or 28° intervals between 18° and 156°, and with solutions of nitric, hydrochloric, and sulphuric acids at 218°, 260°, and 306°. The final values will be found in tables 108 and 109, section 95. Some of these have been plotted in figure 18, on page 266.

The general conclusions to be drawn from the results may be stated as follows:

The equivalent conductance of completely ionized acids, which has already been shown by Noyes and Cooper to approach that of neutral salts up to 218° continues to do so up to at least 306°, where, for example, the ratio of that for hydrochloric acid to that for potassium chloride has become 1.27 (instead of 2.91 at 18° and 1.53 at 218°).

The equivalent conductance (Λ), and therefore also the ionization (γ), of hydrochloric acid, nitric acid, the barium hydroxide change with the concentration (C) according to the same empirical law, $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$ or $C(1 - \gamma) = K(C\gamma)^n$ with n approximately 1.5, as holds true in the case of salts. The ionization of all of them (see tables 114 and 115, section 97) decreases steadily with the temperature, and up to 156° by about the same amount as with neutral salts of the same ionic type; the same is true of hydrochloric acid up to 306°, but the ionization of nitric acid between 218° and 306° decreases much more rapidly, so that it is only 33 per cent instead of about 60 per cent in 0.08 normal solution at 306°.

Dilute nitric acid at 218° and 306° exhibited a somewhat remarkable chemical behavior, in that it sometimes underwent almost complete decomposition, apparently into nitrogen (or nitrous oxide), oxygen, and water, when this decomposition once got started through the presence of a minute quantity of some impurity — a behavior analogous to that observed in the case of silver nitrate by Noyes and Melcher.

Phosphoric acid, which is only moderately ionized, shows a behavior with respect to change with the concentration which is intermediate between that of the largely ionized acids and salts and that required by the mass-action law, the value of the exponent *n* in the concentration function being 1.8 – 1.9. Its ionization decreases rapidly with rising temperature (in 0.1 normal solution from 28.5 per cent at 18° to 17.5 at 100° and 11.5 at 156°); but this does not seem to be accompanied by a closer conformity to the mass-action law. Its ionization-constants calculated by that law (which vary considerably with the dilution) are at 0.1 normal $11,400 \times 10^{-6}$ at 18°, $3,700 \times 10^{-6}$ at 100°, and $1,490 \times 10^{-6}$ at 156°, the values for acetic acid and for chloracetic acid at 25° being 18×10^{-6} and $1,550 \times 10^{-6}$ as determined by Ostwald.

The interpretation of the results obtained with sulphuric acid is complicated by the fact that the ionization doubtless takes place in two stages; but it has been shown that it is possible to determine the hydrogen-ion concentration within fairly narrow limits from the conductance alone, without knowledge of the extent to which the separate stages occur. The ratio of the hydrogen-ion to the total hydrogen of the acid is thus found to vary in 0.08 normal solution from about 66 per cent at 18° to 48 at 100° and 35 at 306°. Similar calculations of the hydrogen-ion concentration have been made in the case of potassium hydrogen sulphate. These show that in 0.1 molal solution at 156° the hydrogen-ion concentration is not more than 3 per cent; and this justifies the conclusion that the secondary ionization of sulphuric acid (into hydrogen-ion and sulphate-ion) in its own moderately concentrated solutions is also insignificant at this temperature and higher temperatures. Interpreted with the help of this conclusion, the conductivity data for the acid show that the primary dissociation (into hydrogen-ion and hydrosulphate-ion) is about the same as that of hydrochloric acid at temperatures between 100° and 306°; and it is reasonable to suppose that the same is true at lower temperatures down to 18°. With the help of this principle the ionization of the hydrosulphate-ion at 18°, 100°, and 156° in the solutions both of the acid and acid salt has been computed; the final results will be found in tables 118 and 119, in section 97. This ionization is thus found to be large at 18°; but it decreases very rapidly with the temperature. Thus in a 0.1 molal potassium hydrogen sulphate solution equal quantities of sulphate-ion and hydrosulphate-ion are present; while at 100° there is only 15 per cent, and at 156°, 4 per cent, as much sulphate-ion as hydrosulphate-ion in the solution. Only rough values of the ionization-constant of the hydrosulphate-ion into hydrogen-ion and sulphate-ion can be given, since they vary very much with the concentration: some idea of its magnitude is furnished by the following values which hold at about 0.01 molal (or 0.002 molal at 156°); $18{,}500 \times 10^{-6}$ at 18°, 1.220×10^{-6} at 100°, and 115×10^{-6} at 156°, whereas the ionization-constant for acetic acid at 18° is 18×10^{-6}. From the change of the ionization-constant with the temperature, the heat absorbed (ΔU) by the reaction $HSO_4^- = H^+ + SO_4^=$ has been found to be given by the expression: $\Delta U = 14{,}170 - 65\,T$, where T represents the absolute temperature. From this it follows that the value at 18° is $-4{,}750$ calories and at 100°, $-10{,}070$ calories, while from Thomsen's heat-of-neutralization measurements and our ionization data the value $-5{,}020$ calories is derived.

PART IX.

IONIZATION OF WATER AT 0°, 18°, AND 25° DERIVED FROM CONDUCTIVITY MEASUREMENTS OF THE HYDROLYSIS OF THE AMMONIUM SALT OF DIKETOTETRAHYDROTHIAZOLE.

BY C. W. KANOLT.

PART IX.

IONIZATION OF WATER AT 0°, 18°, AND 25° DERIVED FROM CONDUCTIVITY MEASUREMENTS OF THE HYDROLYSIS OF THE AMMONIUM SALT OF DIKETOTETRAHYDROTHIAZOLE.

99. OUTLINE OF THE INVESTIGATION.

The degree of ionization of water at ordinary temperatures has been determined by a number of different methods — namely (1) from the hydrolysis of sodium acetate* as derived from the rate at which it saponifies an ester,† and from that of aniline acetate‡ as derived from conductivity measurements § ; (2) from the rate of saponification of methyl acetate by water itself || ; (3) from the electromotive force of the alkali-acid hydrogen cell ¶ ; and (4) from the conductivity of the purest water thus far obtained.** Although these entirely independent measurements have all given for the ionization of water values of the same order of magnitude and have thereby furnished one of the most striking evidences of the Ionic Theory, yet for none of the values so obtained can any considerable percentage accuracy be claimed. It has therefore seemed advisable to make a special study of this constant at ordinary temperatures by the same method that has been employed at higher temperatures by Noyes and Kato (see Part VI) and by Sosman (Part VII), that is, by measuring the increase in conductance produced by adding to a partially hydrolyzed salt of a weak acid and a weak base an excess of the acid or of the base, whereby the hydrolysis is reduced.

In calculating from such data the ionization of water a knowledge of the ionization-constants of the acid and the base and of the degree of ionization of the salt is also necessary.

The salt selected for this purpose must be sufficiently hydrolyzed to give rise to a marked change in the unhydrolyzed portion of it when the excess of acid or base is added. On the other hand, both the acid and base of the salt must be strong enough to permit their ionization-constants to be directly and accurately determined by conductivity measurements. An examination of the available substances previously investigated seemed to show that ammonium hydroxide was the most suitable base, and that

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*Arrhenius, Z. phys. Chem., **11**, 822 (1893).

†Shields, ibid., **12**, 184 (1893).

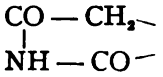
‡Arrhenius, ibid., **5**, 19 (1890); Bredig, ibid., **11**, 829 (1893).

§Walker, ibid., **4**, 334 (1889).

||Wijs, ibid., **11**, 492 (1893).

¶Ostwald, ibid., **11**, 521 (1893); Nernst, ibid., **14**, 155 (1894); Löwenherz, ibid., **20**, 293 (1896).

Kohlrausch and Heydweiller, ibid., **14, 330 (1894).

diketotetrahydrothiazole was the most suitable acid. This acid has also been called dioxythiazole and mustard-oil acetic acid, and has, according to the investigation of Hantzsch,* the structure†  $\begin{array}{l} CO - CH_2 \\ | \\ NH - CO \end{array} \!\!> S$. The base has at 25° an ionization-constant of 18.1×10^{-6} and the acid one of 0.181×10^{-6}, and their salt a hydrolysis of about 4 per cent, as the measurements presented below show. This base is more easily obtained pure than any other base of similar strength; and the acid can be readily prepared in quantity from thiourea and chloracetic acid. It is, however, so weak, that its salt is about ten times as much hydrolyzed as ammonium acetate (which is 0.4 per cent hydrolyzed at 25°); and yet it is strong enough to have a conductance which can be fairly accurately determined, though it lies near the limit in this respect.

In detail, therefore, this investigation has consisted in the preparation and purification of the diketotetrahydrothiazole and the determination of its ionization by conductivity measurements at 0°, 18°, and 25° at various concentrations, in corresponding measurements with ammonium hydroxide, and in measurements at these three temperatures of the conductance of the salt at 0.02 and 0.05 normal both in water alone and in the presence of about the equivalent amount and half the equivalent amount of the free acid and of the free base in separate experiments. In order to determine the conductance of the completely ionized acid and salt, measurements were also made with the latter at a concentration of 0.002 normal.

100. PREPARATION OF THE SUBSTANCES AND SOLUTIONS.

The diketotetrahydrothiazole was prepared as described by Volhard‡ by heating together thiourea and chloracetic acid in aqueous solution. The product was purified by a large number of crystallizations from methyl alcohol and from water. No boneblack was used. The crystallization from water was continued until the sample was perfectly white and no further change in conductance was produced, as will be shown in section 102. The last crystallizations were made from conductivity water in platinum vessels, and the crystals were filtered out and dried at 100° in a platinum Gooch crucible in purified air. A portion of the product so dried was finely powdered and kept in a desiccator over sulphuric acid for several weeks; it lost only a few hundredths of 1 per cent in weight, showing that it was dry. The melting-point of the purified sample was found to be 123.4°.

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*Ber. d. chem. Ges., **20**, 3129 (1887).

†Even assuming that this substance exists in part in the desmotropic "enol" form, this would make no difference in the values of the ionization of water derived from the study of its equilibria; for the concentrations of the two forms must be under all circumstances proportional to each other.

‡J. prakt. Chem. (2) **9**, 6 (1874).

The solutions of the acid were always prepared just before the conductance was measured by dissolving weighed portions of it in a known weight of conductivity water in a Jena flask. The solutions were prepared and transferred to the conductivity vessel in contact with only purified air. The water used for dissolving the acid, and in general throughout this investigation, had at 18° a specific conductance which always lay between 0.15 and 0.60×10^{-6} reciprocal ohms. The solutions of the acid even when kept for several hours in the conductivity-vessel showed a change in conductance of not more than 0.1 per cent.

The ammonium hydroxide solution used was an approximately 0.1 normal one made by diluting with conductivity water a special sample of strong ammonia water (spec. grav., 0.90) furnished by the Baker & Adamson Chemical Co. and certified to be free from amines, carbonates, and silicates. The solution was titrated by running a slight excess of it directly into a known weight of standard hydrochloric acid, and running back to the end-point with hydrochloric acid with the help of methyl orange. The solutions were all measured by weight, not by volume. The hydrochloric acid was itself standardized by precipitating a known weight of it with silver nitrate and weighing the silver chloride. The solution was kept in a two-liter "non-sol" bottle (furnished by Whitall, Tatum & Co.). To protect it from evaporation and contamination it was connected through another bottle of ammonium hydroxide solution of the same strength with a long soda-lime tube through which air was admitted when samples were withdrawn. The solution was transferred through delivery tubes into the conductivity vessel or into a Jena flask in which it was diluted or mixed with the acid solution, in contact with only purified air. In order to use comparatively fresh solutions for the measurements, a new stock solution was prepared in the same way in the course of the experiments, so that the solution employed was never more than ten days old. Determinations of the alkaline strength showed that during this period the change in it was less than 0.1 per cent. The conductance of this solution was found to be substantially identical with that of one prepared from liquid ammonia by Mr. R. B. Sosman.

The solutions of the salt, both alone and with an excess af acid or base, were prepared by introducing into a Jena flask provided with a perforated ground-glass stopper and filled with purified air a weighed quantity of the solid acid, and then introducing without opening the flask the proper quantity of conductivity water and of the stock ammonium hydroxide solution to produce as nearly as possible any desired round concentrations. These were in general attained within 0.1 or 0.2 per cent, but the exact concentration was always considered.

The content by weight of the various solutions obtained as above described was reduced to volume concentration by means of the density of the solution, which in the case of the acid or salt solutions was calculated from the densities of the solid acid and of the water or ammonium hydroxide solution, under the assumption that no change in the total volume occurs on mixing.* The concentration given in the tables below is always that at the temperature of the measurement.

The atomic weights used were those referred to oxygen as 16.00 as given in the report of the International Committee for 1906.† All weights were corrected for the bouyancy of the air.

101. APPARATUS AND METHOD.

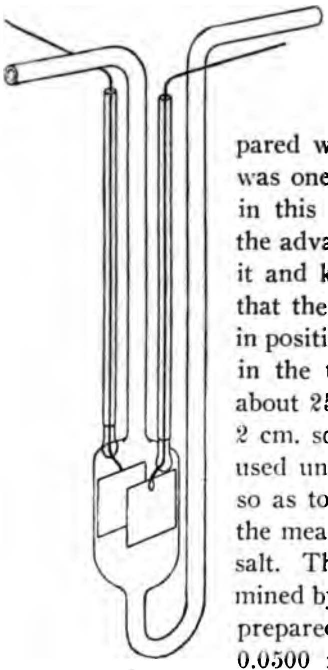

Fig. 19.

The conductivity measurements were made with a slide-wire bridge by the usual Kohlrausch method. The slide-wire was calibrated and the resistance coils were compared with each other. The conductivity vessel used was one of pipette form devised by Mr. G. A. Abbott in this laboratory. It is shown in Fig. 19. It has the advantages that the solution can be introduced into it and kept in it entirely out of contact with the air, that the electrodes are fully protected against change in position, and that the vessel can be entirely immersed in the thermostat. The capacity of the vessel was about 25 c.cm.; and the vertical electrodes were about 2 cm. square and 1.3 cm. apart. The electrodes were used unplatinized in the measurements with the acid, so as to reduce contamination; but were platinized in the measurements with the better-conducting base and salt. The conductance-capacity of the vessel was determined by measuring in it (when unplatinized) a freshly prepared 0.002136 normal or (when platinized) a 0.0500 normal solution of potassium chloride,‡ and allowing for the conductance of the water employed.

The vessel was immersed in well-stirred thermostats whose temperature was kept constant within 0.01°. That at 0° was maintained by a mixture of water and finely crushed ice in large proportion. The thermometers used were compared with the laboratory standard.

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*The density of the acid at 25° was found to be 1.673 by weighing a large excess of it in a pycnometer under its saturated solution. That there was in fact no appreciable volume-change on mixing was shown by direct measurements of the density of known solutions of the acid and of its salt.

†See J. Am. Chem. Soc., **28**, 1 (1906).

‡The actual conductances of these solutions in the vessel after allowing for the conductance of the water were 0.0015095 and 0.03256 reciprocal ohms at 18°, which correspond to conductance-capacities of 0.17861 and 0.17775, respectively, using Kohlrausch and Maltby's equivalent-conductance values. The same value was obtained at the end of the measurements as at the start.

The final bridge reading was not recorded until it had become constant, which it did in 15 – 30 minutes. It then remained constant, even over night, in almost all cases; but with a few solutions containing the salt with an excess of ammonium hydroxide there was a slight progressive increase in conductance, for which a small correction (never more than 0.25 per cent) was applied, depending upon the time which had elapsed before the reading and upon the temperature to which the cell had been exposed.

102. THE CONDUCTIVITY AND IONIZATION-CONSTANTS OF AMMONIUM HYDROXIDE AND DIKETOTETRAHYDROTHIAZOLE.

Tables 120 and 121 contain the results of the conductance measurements with ammonium hydroxide and with diketotetrahydrothiazole. The first column gives the temperature; the second, the date; the third, the concentration in equivalents per liter of solution at the temperature of the measurement; the fourth, the conductance in reciprocal ohms as actually measured in the conductivity vessel, multiplied by 10^6; the fifth, the same diminished by the conductance of the water; the sixth, the equivalent conductance (Λ) calculated by multiplying the values of the preceding column by the conductance-capacity (0.17861 for the acid and 0.17775 for the base) and dividing by the concentration given in the third column and by 10^3; and the seventh, the ionization-constant (K) calculated by the expression $K = \frac{\Lambda^2 C}{\Lambda_0(\Lambda_0 - \Lambda)}$ and multiplied by 10^6.

The values of Λ_0 (the equivalent conductance for complete ionization) used in the calculation of the ionization-constant were derived as follows. That for the OH^- ion at 18° was found to be 173.0 by subtracting Kohlrausch's value[*] for the sodium ion (43.55) from Noyes and Kato's value for sodium hydroxide (216.5, see Part VI). That for the NH^+_4 ion at 18° was found to be 65.4 by subtracting Kohlrausch's value for chloride ion (65.44) from Sosman's value for ammonium chloride (130.9, see Part VII). In this way the value for ammonium hydroxide was found to be 238.4 at 18°. Those for ammonium hydroxide at 0° and 25° were obtained from the corresponding equivalent conductances of the NH^+_4 and OH^- ions at 18° by means of the temperature-coefficients for the conductivities of these ions derived by Kohlrausch.[†] The values so obtained are $\Lambda_{NH_4} = 39.3$, $\Lambda_{OH} = 117.7$ and $\Lambda_{0(NH_4OH)} = 157.0$ at 0°; and $\Lambda_{NH_4} = 75.9$, $\Lambda_{OH} = 194.7$ and $\Lambda_{0(NH_4OH)} = 270.6$ at 25°. The Λ_0 values for the acid at each temperature were obtained from those for its ammonium salt by subtracting the equivalent conductance of the NH^+_4 ion

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[*] Sitzungsber. preuss. Akad. der Wissensch., 1901, 1026-1033.

[†] Ibid., 1901, 10. These coefficients are:

$$(\Lambda_{NH_4})_t = (\Lambda_{NH_4})_{18}\ [1 + 0.0223\ (t - 18) + 0.000079\ (t - 18)^2]$$
$$(\Lambda_{OH})_t = (\Lambda_{OH})_{18}\ [1 + 0.0179\ (t - 18) + 0.000008\ (t - 18)^2]$$
$$(\Lambda_H)_t = (\Lambda_H)_{18}\ [1 + 0.0154\ (t - 18) - 0.000033\ (t - 18)^2]$$

derived as just described, and adding that of the H⁺ ion. The Λ_0-values for the ammonium salt were derived from direct conductance measurements which will be presented and discussed in section 103. For the equivalent conductance of the H⁺ ion at 18° the value (315) derived from the measurements of Goodwin and Haskell* upon very dilute acid solutions was adopted; while at 0° and 25° the values 224.3 and 348.5, respectively, were obtained from this one at 18° by means of Kohlrausch's temperature-coefficients just referred to.

TABLE 120.—*Equivalent conductance and ionization-constant of diketotetrahydrothiazole.*

Temperature.	Date.	Equivalents per liter.	Conductance × 10⁶.		Equivalent conductance.	Ionization-constant × 10⁶.		
			Observed.	Corrected.		Separate values.	Mean values.	
	1906							
0	May 24..	0.2503	185.9	184.5	0.1316	0.0710	0.0709	0.0711
	May 21..	0.1251	131.0	129.7	0.1852	0.0703		
	May 25..	0.1251	132.3	131.2	0.1873	0.0720		
	May 22..	0.0626	92.9	91.6	0.2613	0.0701		
	June 1..	0.2503	185.7	184.7	0.1318	0.0712	0.0713	
	June 2..	0.2503	187.1	186.1	0.1328	0.0723		
	May 30..	0.1251	130.6	128.9	0.1840	0.0694		
	June 5..	0.0626	94.0	93.2	0.2659	0.0725		
18	May 24..	0.2500	372.5	370.1	0.2644	0.1436	0.1463	0.1459
	May 21..	0.1250	266.1	263.9	0.3770	0.1460		
	May 25..	0.1250	268.0	266.2	0.3803	0.1487		
	May 22..	0.0625	189.5	187.2	0.5349	0.1471		
	June 1..	0.2500	371.5	369.9	0.2643	0.1435	0.1455	
	June 2..	0.2500	373.3	371.6	0.2654	0.1447		
	May 30..	0.1250	264.8	261.9	0.3740	0.1437		
	June 5..	0.0625	190.8	189.3	0.5410	0.1504		
25	May 24..	0.2496	463.7	460.7	0.3297	0.1780	0.1818	0.1814
	May 21..	0.1248	330.5	328.0	0.4693	0.1804		
	May 25..	0.1248	333.1	331.0	0.4737	0.1838		
	May 22..	0.0624	237.5	234.8	0.6719	0.1850		
	June 1..	0.2496	462.6	460.7	0.3297	0.1780	0.1811	
	June 2..	0.2496	462.6	460.6	0.3296	0.1779		
	May 30..	0.1248	331.5	328.1	0.4701	0.1810		
	June 5..	0.0624	238.3	236.6	0.6772	0.1876		

TABLE 121.—*Equivalent conductance of ionization-constant of ammonium hydroxide.*

Temperature.	Date.	Equivalents per liter.	Conductance × 10⁶.		Equivalent conductance.	Ionization-constant × 10⁶.	
			Observed.	Corrected.		Separate values.	Mean values.
	1906						
0	July 22..	0.09569	1,015	1,014	1.884	13.95	13.91
	July 24..	0.04540	696	695	2.722	13.88	
18	July 22..	0.09557	1,709	1,708	3.177	17.21	17.15
	July 24..	0.04534	1,171	1,170	4.584	17.09	
25	July 22..	0.09542	1,989	1,988	3.703	18.11	18.06
	July 24..	0.04527	1,363	1,362	5.436	18.02	

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*Phys. Rev., **19**, 386 (1904).

The measurements of May 30 to June 5, given in table 120, were made with a sample of the acid obtained by recrystallizing three times from conductivity water with the usual precautions the material used in these measurements of May 21 – 25. The agreement of the results with the two samples shows that the material underwent no change in the three crystallizations. Ostwald* obtained the value 0.24×10^{-6} for the constant at 25° without using special precautions.

Sosman (see Part VII) with solutions prepared both from liquid ammonia and from the pure ammonia water, obtained for the constant of ammonium hydroxide at 18°, as the mean of a large number of determinations at concentrations from 0.01 to 0.1, the value 17.15×10^{-6}, which is identical with that given in table 121. He obtained the value 17.9×16^{-6} as the means of two determinations at 25°. This value agrees closely with the value 18.06×10^{-6} here presented. Earlier investigators† obtained considerably higher results, partly owing to the incomplete elimination of impurities and to the use of other values of the equivalent conductance for complete ionization.

The results given in the tables show that the constants of the two substances do not vary considerably with the concentration. Sosman, using a much greater range of concentration, also found that the variation of the constant for ammonium hydroxide at 18° was very small.

It will be observed that with rising temperature the ionization of the acid increases very rapidly, and that that of the ammonium hydroxide also increases, but to a much smaller extent.

No reliable estimate of the accuracy of these constants can be made. It seems, however, not improbable that the equivalent-conductance values for the acid may be too high by one per cent, owing to the effect of impurities; and also that its equivalent-conductance values for complete ionization may be in error by one per cent at 18° and 25°, and by even 2-3 per cent at 0°. Under these assumptions the error in its ionization-constant may be 3-4 per cent at 18° and 25°, and 5-7 per cent at 0°. In the case of ammonium hydroxide, although the values of the equivalent conductance at the higher concentrations are probably somewhat more exact than those for the acid, yet there is an even greater uncertainty in the values for complete ionization, so that the ionization-constants are probably of the same order of accuracy.

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*Z. physik. Chem., **3**, 181 (1889).

†Bredig, Z. physik. Chem., **13**, 294 (1894). Davidson, Ber. d. chem. Ges., **31**, 1612 (1898). Hantzsch and Sebaldt, Z. physik. Chem., **30**, 296 (1899).

103. CONDUCTIVITY AND HYDROLYSIS OF THE AMMONIUM SALT OF DIKETOTETRAHYDROTHIAZOLE.

The data relating to the conductivity of the pure ammonium salt are presented in table 122, which is arranged like tables 120 and 121 except that the specific conductance is given in addition to the equivalent conductance.

TABLE 122.—*Conductance of the ammonium salt of diketotetrahydrothiazole.*

Temperature.	Date.	Equivalents per liter.	Conductance × 10^6.		Specific conductance × 10^6.	Equivalent conductance.
			Observed.	Corrected.		
	1906					
0	July 28..	0.05005	14,424	14,423	2,563.6	51.22
	July 29..	0.04997	14,401	14,400	2,559.4	51.22
	July 12..	0.020047	6,015	6,013	1,068.8	53.32
	July 14..	0.020035	6,016	6,014	1,069.3	53.37
	Aug. 3..	0.002143	686.5	685.2	121.8	56.82
18	July 28..	0.04999	22,895	22,893	4,069	81.40
	July 29..	0.04991	22,828	22,826	4,057	81.30
	July 12..	0.020021	9,566	9,563	1,700.0	84.91
	July 14..	0.020010	9,562	9,559	1,699.1	84.91
	Aug 3..	0.002141	1,092.2	1,090.0	193.7	90.50
25	July 28..	0.04992	26,408	26,406	4,694	94.03
	July 29..	0.04983	26,355	26,353	4,684	94.00
	July 12..	0.019992	11,044	11,041	1,962.6	98.17
	July 14..	0.019979	11,033	11,030	1,960.0	98.16
	Aug. 3..	0.002137	1,265.6	1,263.0	224.5	105.04

It will be seen that the values of the equivalent conductance at about the same concentration, which were determined with solutions made up separately from the solid acid and the stock ammonium hydroxide solution, agree in every case within about 0.1 per cent.

For the purpose of facilitating the subsequent calculation of the hydrolysis, the specific conductance $\underline{L}$ has been expressed as a concentration-function of the form $C = \alpha\underline{L} + \beta\underline{L}^{\frac{3}{2}}$ which corresponds to the van't Hoff function $(C\Lambda)^{\frac{3}{2}} = KC(\Lambda_0 - \Lambda)$, which is known to express approximately the variation of the equivalent conductance Λ with the concentration C in the case of neutral salts. As this equation is to be used only for interpolation for a small distance from the values from which it is derived, any possible inaccuracy in the assumed form of the function could not introduce a significant error. Using the conductance values at 0.02 and 0.05 normal as the basis, the corresponding numerical equations are:

$$C = 17.330\ \underline{L} + 43.34\ \underline{L}^{\frac{3}{2}} \text{ at } 0^\circ$$
$$C = 10.832\ \underline{L} + 22.95\ \underline{L}^{\frac{3}{2}} \text{ at } 18^\circ$$
$$C = 9.373\ \underline{L} + 18.45\ \underline{L}^{\frac{3}{2}} \text{ at } 25^\circ$$

Table 123 contains the data for the ammonium salt in the presence of an excess of the free acid or base. The first five columns are self-explanatory.

The sixth column contains the uncorrected specific conductance × 10^6 of the solution in reciprocal ohms obtained by multiplying the observed conductance by the conductance-capacity and by 10^6.

The seventh column contains the corresponding specific conductance corrected by subtracting that of the water and in some cases the small estimated increase due to progressive contamination during the period of the measurement (see section 101).

The eighth column headed "Salt in solution" contains the same values after correcting them for the specific conductance of the ionized ammonium hydroxide, when this was present in excess. (The conductance due to the ionized acid when it was in excess was entirely inappreciable.) This conductance ($\underline{L}_B$) was computed by the equations:

$$C_{OH} = \frac{K_B C_{NH_4OH}}{C_{NH_4}} \cdot = \frac{K_B C_B}{C\gamma}\ ;\ \text{and}\ \underline{L}_B = 10^3\, C_{OH}\,(\Lambda_{NH} + \Lambda_{OH})$$

in which K_B is the ionization-constant for ammonium hydroxide, C_B the excess of it present, and C is the concentration of the salt and γ its degree of ionization.

The ninth column gives the concentration (C_0) at which the salt in water alone has the same specific conductance as that (given in the eighth column) of the salt in the presence of the acid or base; this concentration C_0 was calculated by the empirical relations between C and $\underline{L}$ given on the preceding page.

The last column contains the values of the percentage hydrolysis ($100h_0$) of the salt in water alone at the concentration C_0. These values have been computed by means of the equation:

$$h_0 = \frac{C_0 - C}{C_0}\,\frac{C_B - (C_0 - C)}{C_B - 2\,(C_0 - C)}$$

in which C represents the concentration of the salt in the mixture and C_B that of the added base (or acid). This equation results from combination of the two equations:

$$C_0(1 - h_0) = C(1 - h)$$
$$(C_0 h_0)^2 = Ch(Ch + C_B)$$

in which h represents the hydrolysis of the salt in the presence of the excess of base (or acid). The first of these, which states that the concentration of the unhydrolyzed portion (which is equal to the sum of the concentrations of the ions and the un-ionized salt) is the same in the two cases, is a consequence of the definition of C_0. The second of these equations is the expression of the mass-action requirement that the product of the concentrations of the free acid and base be the same when the ion-concentrations are the same.

TABLE 123.—*Conductance of the salt with an excess of acid or base and its hydrolysis.*

Temperature.	Date.	Milli-equivalents per liter.			Specific conductance × 10^6.			Concentration (C_0) of salt in water alone.	Percentage hydrolysis ($100h_0$)
					Solution.		Salt in solution.		
		Salt.	Acid.	Base.	Observed.	Corrected.			
	1906								
0	July 10.	20.025	......	10.95	1,099.8	1,096.8	1,095.5	20.555	2.71
	July 11.	20.025	......	19.78	1,100.6	1,098.4	1,096.0	20.562	2.68
	July 15.	20.068	19.96	......	1,100.5	1,100.3	1,100.3	20.644	2.87
	July 16.	20.068	10.13	......	1,099.8	1,099.5	1,099.5	20.629	2.88
								Mean ..	2.78
								a. d.....	0.09
	July 26.	50.06	......	24.60	2,622.9	2,621.7	2,620.4	51.22	2.37
	July 27.	50.06	......	45.29	2,632.7	2,631.7	2,629.2	51.39	*2.66
	July 30.	50.10	49.14	.....	2,622.9	2,622.6	2,622.6	51.27	2.34
	July 31.	50.10	24.45	......	2,623.3	2,623.0	2,623.0	51.27	2.40
								Mean ..	2.37
								a. d.....	0.02
18	July 10.	20.000	......	10.93	1,765.4	1,761.2	1,758.8	20.742	3.82
	July 11.	20.000	......	19.75	1,767.6	1,764.6	1,760.1	20.751	3.76
	July 15.	20.044	19.94	......	1,767.4	1,767.0	1,767.0	20.836	3.95
	July 16.	20.044	10.12	......	1,766.4	1,765.9	1,765.9	20.821	4.04
								Mean ..	3.89
								a. d.....	0.10
	July 26.	50.00	......	24.57	4,200.0	4,194.1	4,191.6	51.63	3.38
	July 27.	50.00	......	45.23	4,215.3	4,210.3	4,205.5	51.80	*3.61
	July 30.	50.04	49.08	......	4,201.3	4,200.9	4,200.9	51.74	3.41
	July 31.	50.04	24.43	......	4,195.9	4,195.5	4,195.5	51.68	3.39
								Mean ..	3.39
								a. d.....	0.01
25	July 10.	19.968	......	10.91	2,042.2	2,039.6	2,036.6	20.784	4.25
	July 11.	19.968	......	19.73	2,047.6	2,045.4	2,040.0	20.818	4.24
	July 15.	20.013	19.91	......	2,050.9	2,050.4	2,050.4	20.921	4.52
	July 16.	20.013	10.10	......	2,047.4	2,046.8	2,046.8	20.884	4.58
								Mean ..	4.40
								a. d.....	0.15
	July 26.	49.92	......	24.53	4,873.9	4,861.7	4,858.7	51.80	3.94
	July 27.	49.92	......	45.17	4,894.7	4,885.1	4,879.4	52.02	*4.22
	July 30.	49.96	49.01	......	4,866.4	4,865.9	4,865.9	51.88	3.85
	July 31.	49.96	24.39	......	4,859.9	4,859.4	4,859.4	51.81	3.86
								Mean ..	3.88
								a. d.....	0.04

*Omitted in the computation of the mean.

It will be seen from the last column of table 123 that the values of a. d. (the average deviation of the separate hydrolysis values from the mean) are about 0.10 at 0° and 18°, and 0.15 at 25° for the more dilute salt solution. The deviations for the more concentrated salt solution are much less than these. It is to be remembered in this connection that these hydrolysis values are derived from experiments in some of which an excess of acid, and in others of which an excess of base was present, and in which varying quantities of these were added, and that most constant errors would either have been eliminated in the difference in the measurements with the mixture and the pure salt, or would have shown themselves by producing opposite effects when the acid and base were in excess.

Before calculating the hydrolysis-constant, it is necessary to determine the ionization of the salt at the concentrations in question, and therefore to determine the equivalent conductance Λ_0 for complete ionization. To do this the equivalent conductance of the unhydrolyzed part of the salt has been calculated at the three concentrations at which measurements were made by dividing the specific conductance as given in table 123 by the concentration of the unhydrolyzed part $C_0(1-h_0)$; and evidently it is to this concentration that the so-obtained values of the equivalent conductance refer. The values for h_0 used at 0.02 and 0.05 normal were the means given in table 123. The value of h_0 used for the more dilute solution was calculated from these by the mass-action formula given below. From these three values of Λ the values of the three constants n, K, and Λ_0 in the empirical equation, $(\Lambda C)^n = K(\Lambda_0 - \Lambda)C$, were computed. The ionization of the salt was then obtained by dividing the Λ-values by this value of Λ_0.

Table 124 contains the so-derived values of the equivalent conductance and percentage ionization of the salt. The values of the exponent n were found to be 1.35 at 0°, 1.39 at 18°, and 1.35 at 25°, thus of about the same magnitude as for ordinary salts. The ionization will also be seen to be about the same as that of other salts of the same ionic type.

TABLE 124.—*Equivalent conductance and ionization of the unhydrolyzed ammonium salt.*

Temperature.	Equivalents per liter.	Equivalent conductance.	Percentage ionization.
0	0.04875	52.55	84.5
	0.01950	54.81	88.1
	0.002080	58.5	94.1
	0.00	62.2	....
18	0.04816	84.38	85.0
	0.01926	88.22	88.8
	0.002055	94.3	94.9
	0.00	99.3	....
25	0.04782	98.03	83.1
	0.01913	102.54	87.0
	0.002035	110.1	93.4
	0.00	117.9	....

From the values of the hydrolysis and ionization given in tables 123 and 124, the hydrolysis-constant K_H (equal to $\sqrt{\frac{K_W}{K_A K_B}}$) can be readily calculated by the mass-action relation $\frac{h_0}{(1-h_0)\gamma} = K_H$, in which h_0 represents the hydrolysis of the salt in water alone at any concentration C_0, γ is the fraction of the unhydrolyzed salt $C_0\ (1-h_0)$ which exists as ions, and K_W, K_A and K_B are the ionization-constants for water, the acid, and the base, respectively. This equation is readily derived by combining the three simple mass-action equations, $C_H C_{OH} = K_W$, $C_H\ C_A = K_A C_{HA}$, and $C_B\ C_{OH} = K_B C_{BOH}$, substituting for C_B and C_A the expression $C_0(1-h_0)\gamma$ and for C_{HA} and C_{BOH} the expression $C_0 h_0$, and taking the square root. The values of the hydrolysis constant K_H thus calculated are given in table 125. The values at the two concentrations will be seen to differ by from 12 to 9 per cent. As those at the higher concentration are influenced to a less extent by impurities and contamination, a double weight has been assigned to them in deriving the final mean values. It is not improbable that these values are still too high; but it is unlikely that the error exceeds 5 per cent.

TABLE 125.—*The hydrolysis-constant for the ammonium salt.*

Temperature.	Equivalents per liter.	Hydrolysis-constant.	
		Separate values.	Mean values.
0	0.05	0.0287	0.0299
	0.02	0.0324	
18	0.05	0.0413	0.0427
	0.02	0.0456	
25	0.05	0.0486	0.0500
	0.02	0.0529	

104. THE IONIZATION OF WATER.

The ionization-constants of water ($K_W = C_H\ C_{OH}$) can be calculated from the hydrolysis-constants given in table 125, and the ionization-constants of the acid and base given in section 102. Table 126 contains the values of this constant for water, and also those of its square-root, which last represent the concentration of the hydrogen and hydroxide ion in pure water (in equivalents per liter).

TABLE 126.—*The ionization-constant of water and the hydrogen or hydroxide-ion concentration.*

Temperature.	Ionization-constant $K_W \times 10^{14}$.	Ion concentration. $(\sqrt{K_W}=C_H=C_{OH})\times 10^7$.
0	0.089	0.30
18	0.46	0.68
25	0.82	0.91

To compare these results with those previously obtained the various values for the hydrogen-ion or hydroxide-ion concentration in pure water have been brought together in table 127.

TABLE 127.—*The hydrogen-ion concentration* ($\times 10^7$) *in pure water. Results of various investigators.*[*]

Investigator.	Method of determination.	0°.	18°.	25°.
Arrhenius......	Hydrolysis of sodium acetate by ester-saponification	......	......	1.1
Wijs...........	Catalysis of ester by pure water	......	......	1.2
Nernst	Electromotive force of gas cell	......	0.8	......
Löwenherz	Electromotive force of gas cell	......	......	1.19
Kohlrausch & Heydweiller..	Conductance of pure water	0.36	0.80	1.06
Kanolt.........	Hydrolysis	0.30	0.68	0.91

[*] For references to their articles see section 99.

It will be seen that the new values are uniformly lower than those of Kohlrausch and Heydweiller, but only by from 16 to 20 per cent. This approximate agreement is of interest not only in indicating the absence of any considerable error in the values of Kohlrausch and Heydweiller, in spite of the somewhat uncertain correction that had to be applied for the impurities in the water; but also in proving that the ionization of water is nearly, if not quite, the same when pure, as it is when an ionized salt is present in it at a concentration of 0.02 to 0.05 normal.

As the most probable values of the hydrogen-ion concentration in pure water it would seem best to adopt for the present the lower ones derived above; for, although it is not impossible that these are in error by as much as 10 per cent, yet it is reasonably certain that the error lies in such a direction as to produce too high rather than too low results. This will be evident when it is considered that the effect of impurities in the water or the solutes would be to give rise not only to too high values for the ionization-constants of the acid and base, but also, by combining with the excess of either of them added in the hydrolysis experiments, to give too great an increase in the conductance and therefore too great a value for the hydrolysis.

It will be seen from table 126 that the hydrogen-ion concentration increases with great rapidity with the temperature, being three times as great at 25° as at 0°. It is of interest to calculate from this increase the heat of ionization of water, and to compare its value with that obtained for the heat of neutralization of strong acids and bases. The calculation has been made for the two temperature-intervals by the equation

$$\log_e \frac{K_2}{K_1} = \frac{Q}{R} \frac{T_2 - T_1}{T_1 T_2}$$

where K_1 and K_2 represent the ionization-constants of water at T_1 and T_2, R is the gas-constant (1.986 cal per degree), and Q is the heat of ionization of one mol of water. The value of Q is thus found to be 14,500 calories at 9°, and 14,200 calories at 21.5°. The mean value of the heats of neutralization of potassium and sodium hydroxides by hydrochloric and nitric acids as recently determined by Wörmann* is 14,240 calories at 9° and 13,590 calories at 21.5°. The agreement is a surprisingly close one, and shows that the ionization values at the three temperatures, if affected by errors, must be affected by them by the same percentage amount.

105. SUMMARY.

In this article have been presented the results of measurements of the conductivity at 0°, 18°, and 25° of ammonium hydroxide, diketotetrahydrothiazole, and of the salt of this base and acid, both alone and in the presence of an excess of the base or acid. From these measurements have been calculated the ionization-constants of the base and acid, the hydrolysis and hydrolysis-constant of the salt, the ionization-constant of water and the concentration of the hydrogen-ion or hydroxide-ion in it. The final results may be summarized as follows:

TABLE 128.—*Ionization-constants of ammonium hydroxide, of diketotetrahydrothiazole, and of water.*

Temperature.	Ionization-constants.			Concentration of hydrogen-ion in pure water.
	Ammonium hydroxide.	Diketotetrahydrothiazole.	Water.	
0	13.91×10^{-6}	0.0711×10^{-6}	0.089×10^{-14}	0.30×10^{-7}
18	17.15×10^{-6}	0.146×10^{-6}	0.46×10^{-14}	0.68×10^{-7}
25	18.06×10^{-6}	0.181×10^{-6}	0.82×10^{-14}	0.91×10^{-7}

The values for the hydrogen-ion concentration given in the last column are 16 to 20 per cent lower than those derived by Kohlrausch and Heydweiller from the conductivity of the purest water. From their variation with the temperature the heat of ionization of water has been calculated, and found to be in close agreement with the directly measured heat of neutralization of strong acids and bases.

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*Drude's Ann. Phys., **18**, 793 (1905).

PART X.

SOLUBILITY OF SILVER CHLORIDE, BROMIDE, AND SULPHOCYANATE AT 100°.

BY WILLIAM BÖTTGER.

PART X.

SOLUBILITY OF SILVER CHLORIDE, BROMIDE, AND SULPHOCYANATE AT 100°.

106. OUTLINE OF THE INVESTIGATION.

The solubility of many difficultly soluble salts at room temperature has already been determined by several investigators* by means of measurements of the electrical conductivity of the saturated solutions. The extension of such measurements to much higher temperatures is attended with the difficulties that open vessels can not be used owing to evaporation of the solvent, and that glass vessels are inadmissible owing to the contamination of the solution resulting from them. The platinum-lined bombs with quartz insulation recently constructed in this laboratory and described in Part II, enable, however, such measurements to be made with readiness and accuracy. One of these being placed at my disposal by Professor Noyes, I took the opportunity of making a few solubility determinations at 100°, at which temperature the results have much practical interest, owing to the frequent use of boiling solutions in analytical and preparation work. Unfortunately the time available only permitted the investigation of three salts. The results obtained with these, though not so accurate as might have been secured if the bomb could have been rotated within the bath, as will be done in later investigations in this laboratory, seem, however, to deserve publication.

107. DESCRIPTION OF THE EXPERIMENTS.

The solubility determinations were made in the same bomb that had been used just before by A. A. Noyes and Y. Kato (see Part VI), after certain repairs had been made in it. It was provided with an open cylindrical electrode of platinum-iridium. It was heated for the 100° measurements in the steam-jacketed xylene bath described in section 32, Part IV. The conductance-capacity was determined by measuring in the bomb at 18° the conductance of a 0.005 normal potassium chloride solution and was found to be 0.1490, which was nearly identical with an entirely independent result (0.1492) obtained about the same time by Mr. Kato.

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*F. Kohlrausch and Rose, Z. physik. Chem., **12**, 234; Holleman, ibid., **12**, 125; F. Kohlrausch, ibid., **44**, 197; W. Böttger, ibid., **46**, 521.

Since the determinations of solubility were to be made by measuring the conductance of the saturated solution in the presence of an excess of solid salt, the question arose whether the latter would influence the conductance-capacity appreciably, as it might possibly do by settling out upon the cylindrical electrode or even by remaining in suspension. To answer this question, a 0.01 normal sodium chloride solution was measured in the bomb both at 18° and 100°, first alone and then in the presence of 0.5 to 0.8 c.cm. (measured moist) of solid silver chloride. The conductance of the dissolved portion of the latter salt can be shown by applying the principle of the common-ion effect to the solubility-value hereinafter presented (152×10^{-6} mols per liter at 100°) to be only about 1×10^{-6} reciprocal ohms even at 100°, and therefore to be negligible in comparison with the conductance of the sodium chloride. The specific conductances multiplied by 10^6 observed in these experiments are given in the following table.

Solution.	18°		99.8°.
	Initial.	Final.	
0.01 normal NaCl......	1,024	1,025	3,215
	*1,023	*1,024	*3,213
0.01 normal NaCl + 0.5—0.8 c.cm. solid AgCl	1,020	1,023	3,215
	*1,020	*1,020	*3,214
	......	*1,020	*3,215

*These second and third values were obtained by removing the bomb from the bath, shaking it, returning it, and allowing it to come to the original temperature.

These results show that the effect of the solid salt on the conductance certainly does not exceed 0.4 per cent and it is not improbable that the differences of this magnitude observed at 18° were due to temperature variations, which were not entirely excluded in these first experiments; for the differences at 99.8° where the temperature regulation was automatic seem to be scarcely appreciable. In any case the effect of the solid salt on the conductance-capacity is less than the other errors of the solubility determinations.

The correction for the conductance of the water, which is important in such dilute solutions, was determined as follows, in order to avoid making a new measurement in the bomb at 100° with each new sample of water. Each of two separate samples was measured nearly simultaneously at 46° in the glass apparatus with un-platinized electrodes which I had previously used for solubility experiments* and at 100° in the bomb itself after it had been thoroughly soaked out by heating with pure water at 100°.

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*Z. phys. Chem., **46**, 530 (1903).

The observed specific conductances $\times 10^6$ were as follows:

	At 100°.	At 46°.	Ratio.
Sample 1.....	1.98	1.10	1.80
Sample 2.....	2.48	1.27	1.95
Mean	......	......	1.88

All other samples were measured only at 46°; and their specific conductances in the bomb at 100° were calculated by multiplying the values so obtained by 1.9. The error involved in this method of computation, including that arising from unavoidable accidental contamination* from the air in filling the bomb, would rarely exceed 0.3×10^{-6} reciprocal ohms. The error that might arise from the gradual leaching out of conducting material from the bomb itself was practically eliminated, since the various salts were never introduced into the bomb until it had been so thoroughly soaked out by heating to 100° with pure water that the conductivity increased by only 0.1×10^{-6} reciprocal ohms on removing the bomb from the bath, shaking, and returning it.

The silver chloride, bromide, and sulphocyanate, whose solubilities were determined, were prepared by adding with vigorous stirring a cold 0.1 normal silver nitrate solution to a nearly equivalent quantity of 0.1 normal solution of sodium chloride or hydrochloric acid, potassium bromide, and ammonium sulphocyanate, respectively, which was heated to about 50°. The sodium chloride had been especially purified by precipitation in the usual manner with hydrochloric acid, but the chemically pure salts of trade were used in the other cases. The supernatant liquid was then immediately poured off, and the residue was washed for two weeks with hot water which was renewed several times each day. The salts were prepared and kept in a room illuminated only by red light.

The solubility-determinations were made as follows. When the bomb was found to give off conducting material only within the above-mentioned limit, from 0.5 to 0.8 c.cm. of the moist silver salt was placed in it and washed three times with pure water; then the bomb was filled up to within 5 to 8 mm. of the rim, taking every precaution to avoid contamination by impurities from the air, and it was finally closed. Only a few minutes later, during which time the glass vessel for measuring the conductance of the water at 46° was filled, the conductance of the contents of the bomb was measured at room temperature without shaking the bomb after it was closed. The bomb was then shaken violently to bring about a close contact between solid and liquid, and the conductance was again measured. In most cases this was repeated till only a very slight increase of conductance was observed.*

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*The magnitude of such contamination is illustrated by the fact that three portions from the same stock-bottle successively introduced into the bomb showed at about 25° specific conductances of 1.17, 0.99, and 1.18×10^{-6} reciprocal ohms.

The bomb was then put into the xylene bath heated by steam. When the temperature of the bath had reached its former value, readings were taken every five minutes, and as soon as no appreciable change in the conductivity occurred, the conductivity was measured with three different resistances in the rheostat. The bomb was then taken out of the bath, shaken violently about 100 times, replaced, and readings taken after heating for 40 to 60 minutes.

Since at the end of these operations the specific conductance had increased by about 1×10^{-6}, the change was at first ascribed to incomplete saturation. If this were true, one would expect of course that upon repeated shakings and heatings these increases would become less and less. To test this view an experiment was made with silver chloride in which the observed conductances measured at 99.7° at the start, and after successive shakings and the stated periods of heating between each reading were as follows:

Period of heating (min.)........	0	62	125	56	55
Specific conductance $\times 10^6$......	59.72	60.47	62.73	64.25	65.77
Increase per hour	....	0.72	1.08	1.62	1.68

Considering in connection with these results the fact that even at room temperature the saturation occurs almost instantaneously, it seems very probable that these increases are not due, or are only in small part due, to incomplete saturation; for if they were due to this, one would expect that the increase per hour would diminish instead of increasing. It is more probable that the effect is mainly due to a slight decomposition of the salt — perhaps a reduction by impurities in the water.† It might also conceivably arise from a gradual leaching out of soluble impurities, but this is disproved by experiments that will be described in the next section.

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*These data at the room temperature are not given in the table below, as they were not measured at any one temperature, their purpose being mainly to serve as an indication of accidental contamination in any experiment. As a result of all the observations it was found that the increases after shaking were small in comparison with those taking place immediately after pouring in the water, showing that saturation is attained very rapidly. This is illustrated by the following data. The conductance immediately after closing the bomb at room temperature (22.7°) was 2.754; and after shaking successively the number of times shown by the figures in parentheses it was: (2) 2.922; (2) 2.966; (2) 2.982; (2) 2.985; (4) 3.004; (4) 3.002; (10) 3.011; (10) 3.015; (100) 3.028; (100) 3.028. These numbers show, if we assume 3.03 as the final value corresponding to that temperature and 1.00 to be the conductance of the water, that 86 per cent of the silver chloride goes into solution during the short period of pouring in the water and closing the bomb and 98 per cent after shaking the bomb 8 times. Whether the later increase of 2 per cent is a consequence of further solution of the salt or whether it is due to a rise of temperature brought about by the process of shaking is uncertain.

†It was found in general on bringing the contents of the bomb back to room temperature that the conductance had increased by an amount which was greater the longer the duration of the previous heating. In one case the conductance of the saturated solution at 29.1° before heating was 3.84×10^{-6} reciprocal ohms, while upon returning to that temperature after heating for 60 minutes it had become 4.16×10^{-6}.

The method of heating and shaking just described was used in experiments 1 to 5 (see table 129) with silver chloride and in all of those with silver sulphocyanate. A slightly different procedure was followed in some of the later experiments (6 to 9) with silver chloride and in those with silver bromide, in that the bomb was removed from the bath after the latter had reached about 99° and vigorously shaken *before* the first bridge-reading was taken; after which it was, as before, removed from the bath, well shaken, returned to it, heated again for 30 to 60 minutes, and a new reading taken. Even in this case the agitation took place somewhat below 100°, since the bomb cooled off a little, while it was out of the bath; but it is probable that enough fine particles remained in suspension to secure saturation in the subsequent period of heating. In the last two experiments with silver chloride (10 and 11) the bomb was not shaken before the first reading at 100°, but was heated for an unusually long period of time (135 and 265 minutes, respectively); and afterwards the effect of rocking the bomb gently in the bath was tried.

108. THE CONDUCTIVITY DATA.

The following table contains the results of the measurements. The headings are for the most part self-explanatory. All the conductivity values are those of the specific conductance expressed in reciprocal ohms and multiplied by 10^6. The conductance of the water at 100° was calculated, as stated above, from that at 46° by multiplying by 1.9. The headings "first value" and "second value" under "Specific conductance of solution at t°" will be understood from the description of the procedure in the last section; the "second value" was always that obtained by removing the bomb from the bath after the "first value" was observed, shaking it vigorously, and heating it again for a considerable period. In the last column the time in minutes that the bomb was heated in the 100° bath before the reading for the "first value" was taken, is given under I, and the time between the "first" and "second values" is given under II. In the determinations with silver chloride the sample prepared from silver nitrate and hydrochloric acid was used in experiments 4 and 5, that from silver nitrate and sodium chloride in all the others. In experiments 6 to 9 the same portion of silver chloride was used, being treated successively with fresh portions of water, to see whether the apparent solubility would decrease owing to the leaching out at first of more soluble impurities.

TABLE 129.—*Specific conductance of saturated solutions near 100°.*

Experiment No.	Date.	Specific conductance of water.		Temperature of experiment t°.	Specific conductance of solution at t°		Specific conductance of salt at t°.		Time of heating.	
		At 46°.	At 100° L_W		First value L_1	Second value L_2	L_1-L_W	L_2-L_W	I.	II.
				SILVER CHLORIDE.						
	1905									
1......	July 28..	1.33	2.58	100.1	60.76	61.82	58.18	59.24	80	40
2......	July 29..	1.25	2.38	100.0	60.40	[1]62.16	58.02	59.78	75	60
3......	July 29..	1.50	2.85	99.9	60.54	......	57.69	......	55	.....
4......	July 31..	1.30	2.47	99.7	59.72	[2]60.47	57.25	58.00	80	60
5......	Aug. 1..	1.20	2.28	99.9	60.27	......	57.91	......	60	.....
6......	Aug. 9..	1.86	3.53	100.2	61.72	62.35	58.19	58.82	60	40
7......	Aug. 9..	1.58	3.00	100.2	60.82	61.35	57.82	58.35	55	30
8......	Aug. 9..	1.67	3.17	100.2	61.69	......	58.52	......	60	.....
9......	Aug. 10..	1.75	3.33	100.2	62.20	62.47	58.87	59.14	70	60
10......	Aug. 10..	1.25	2.38	100.2	60.16	......	57.78	......	135	.....
11......	Aug. 11..	1.62	3.08	100.1	[3]61.94	62.27	58.86	59.19	265	60
Mean .	......	......	......	100.06	......	......	58.10	58.93	90	50
a. d...	......	......	......	......	......	......	0.35	0.46	.....	.....
				SILVER SULPHOCYANATE.						
1......	Aug. 3..	1.30	2.47	100.1	17.23	17.65	14.76	15.18	95	30
2......	Aug. 3..	1.47	2.79	100.1	[3]16.91	......	14.12	......	50	.....
3......	Aug. 4..	1.10	2.09	100.1	[3]17.24	......	15.15	......	75	.....
4......	Aug. 4..	1.26	2.39	100.1	[3]17.28	......	14.89	......	50	.....
Mean .	......	......	......	100.10	......	......	14.73	15.18	67	30
a. d...	......	......	......	......	......	......	0.30	......	.....	.....
				SILVER BROMIDE.						
1......	Aug. 7..	1.01	1.92	99.95	10.36	[5]11.46	8.44	[7]9.54	45	[5]25
2......	Aug. 7..	1.20	2.28	[6]99.95	10.89	......	[6]8.61	......	[7]60	.....
3......	Aug. 8..	1.19	2.26	100.1	9.91	10.92	7.65	8.66	55	75
4......	Aug. 8..	1.29	2.45	100.1	[3]10.62	......	8.17	......	60	.....
5......	Aug. 8..	1.37	2.60	100.1	[3]10.34	......	7.74	......	70	.....
Mean ..	......	......	......	100.06	......	......	8.00	8.66	56	75
a. d...	......	......	......	......	......	......	0.30	......	.....	.....

[1] On shaking again and heating for 45 minutes longer the value became 62.87, corresponding to an increase of 0.95 per hour.

[2] For full data on the effect of repeated shaking and heating in this experiment see section II.

[3] These values were obtained after rocking the bomb in the bath. The changes produced by it were, however, not large, except in one case, where the bomb had not been heated long enough. They amounted to + 0.98 in expt. 10 and + 0.16 in expt. 11 with silver chloride, to — 0.16 in expt. 2, + 0.18 in expt. 3, and + 0.16 in expt. 4 with the sulphocyanate; and to + 0.19 in expt. 4 and + 0.09 in expt. 5 with the bromide.

[4] On shaking and heating for 40 minutes longer the value became 62.63 corresponding to an increase of 0.54 per hour.

[5] On shaking and heating for 35 minutes longer the value became 12.19 and after another 60 minutes, 13.28, corresponding to increase of 1.25 and 1.09 per hour.

[6] Omitted in calculating the mean since the measurements at room temperature showed contamination.

[7] Omitted in calculating the mean since the rate of progressive change was abnormally large.

109. FINAL CONDUCTANCE VALUES FOR THE SATURATED SOLUTIONS.

Attention may be first called to the results with the two separate samples of silver chloride. That prepared with hydrochloric acid and used in experiments 4 and 5 gave the mean value 57.58 at 99.80° while the sample made from sodium chloride gave 58.22 at 100.12°. Reduced to a common temperature of 100° by means of the temperature-coefficient 3.7 per cent per degree (see below) these values become 58.01 and 57.96, which are in close agreement.

It may be next pointed out that the four experiments (6 – 9) made successively with the same portion of silver chloride do not show any progressive decrease, the values being 58.19, 57.82, 58.52, 58.87, thus making it improbable that soluble impurities are enclosed within the solid salt and are gradually leaching out.

It is also of some interest to compare the mean value from experiments 1 – 5 with that from experiments 6 – 9, since in the latter, but not in the former, the bomb was shaken after the temperature of the bath had been nearly attained. These two mean values are 57.81 at 99.92°, and 58.35 at 100.20°, which when reduced to 100° become 57.98 and 57.92, respectively, thus confirming the conclusion that saturation was attained in both series.

It will be seen that the variable errors give rise to an average deviation of the separate values from the mean conductivity of the salts of about 0.3×10^{-6} reciprocal ohms in all three cases. Far more serious, however, are probably the constant errors, which may arise from the failure to attain complete saturation in the "first values" at any rate, and from the contamination of the solution by the progressive decomposition of the salt. These two errors would affect the results in opposite directions. It is, however, probable from what has been said above that the former source of error is insignificant in comparison with the latter. The best method of treatment seems to be, therefore, to apply a correction for the progressive increase in conductance. Assuming that complete saturation was attained in the case of the first values $\underline{L}_1 - \underline{L}_w$, then the increase $(\underline{L}_2 - \underline{L}_w) - (\underline{L}_1 - \underline{L}_w)$ is wholly due to progressive contamination, and assuming further that it is proportional to the time, we may obtain a better value by subtracting from $\underline{L}_1 - \underline{L}_w$ the product of this increase by the ratio of the first period of heating* to the second period. In making this calculation, the mean increase per hour was first computed for each salt from all the experiments for which both "first" and "second values" are given in the table.† Correcting in this way the mean of the first values in the table we get the following final results, which have also been corrected to 100° with the help of the van't Hoff equation* and the temperature-coefficient of the conductivity of silver nitrate.†

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*Decreased by ten minutes to allow for the time required to raise the bomb from 20° to 100°.

†This was found to be 0.96 for AgCl, 0.84 for AgSCN, and 0.80 for AgBr. per hour. Compare the values given in foot notes 1, 4, and 5 to table 129.

TABLE 130.—*Specific conductance of the saturated solutions at 100°.*

Salt.	Specific conductance $\times 10^6$.
AgCl	56.7
AgSCN	13.9
AgBr..................	7.4

It seems very improbable that the errors from any source in these final values exceed half the differences between them and the "first values" directly observed. Under this assumption the possible percentage errors are 1.2 for the chloride, 2.9 for the sulphocyanate, and 4.0 for the bromide.

110. THE SOLUBILITY VALUES.

To derive the solubility (in equivalents per cubic centimeter) from these conductance values, it is necessary to divide them by the equivalent conductance (Λ_0) of the salt at zero concentration and at 100°. The Λ_0 value for silver nitrate at 100° has already been determined to be 367 by Mr. A. C. Melcher; and since those for the three silver salts in question are known to differ from this by only 3 to 4½ per cent at 20°‡, and the differences between the mobilities of various ions become less with rising temperature, no error of importance will be made by assuming the Λ_0-values for the three salts to differ from that for the nitrate at 100° by half the percentage amount by which they differ from it at 20°. The Λ_0-values at 100° calculated under this assumption are 373 for AgCl, 359 for AgSCN, and 375 for AgBr.

The solubility values at 100° computed in this way and expressed in milligrams and in equivalents per liter are given in the following table, For comparison the values previously found at 20° and the ratio of the solubility at 100° (S_{100}) to that at 20° (S_{20}) are given in parallel columns. The percentage errors in these 100° solubility values are of the same magnitude as those in the 100° values of the specific conductances. (See end of section 109.)

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* $\frac{dS/S}{dT}=\frac{L}{2RT^2}$, where S is the solubility and L the molal heat of solution, whose values are cited in the next section. $\frac{dS/S}{dT}$ is thus found to be at 100° 2.8 per cent for AgCl, 4.0 per cent for AgSCN, and 3.6 per cent for AgBr.

†This temperature-coefficient has been found by Mr. A. C. Melcher to be 0.88 per cent at 100°. Combining this with the temperature-coefficient of the solubility, we get for the temperature-coefficient of the conductance of the saturated solutions 3.7 per cent for AgCl, 4.9 per cent for AgSCN, and 4.5 per cent for AgBr.

‡See Böttger, Zstchr. phys. Chem., **46**, 596 (1903). The values at 20° are 121.7 for $AgNO_3$, 125.5 for AgCl, 127.1 for AgBr, and 116.1 for AgSCN. Those for the three latter salts differ from that for the nitrate by +3.1 +4.4, and −4.6 per cent, respectively.

TABLE 131.—*Solubility of silver chloride, sulphocyanate, and bromide.*

Salt.	Milligrams per liter at 100°.	Equivalents per liter at 100° × 10^6.	Equivalents per liter at 20° × 10^6.	Ratio S_{100}/S_{20}.
AgCl.....	21.8	152	*11.0 †10.6	13.8 14.3
AgSCN ..	6.4	39	† 0.83	46
AgBr.....	3.7	20	* 0.54 † 0.45	35 42

*Kohlrausch, Z. phys. Chem., **50**, 356 (1905). I have corrected his values to 20° by means of his own temperature-coefficients.
†Böttger, Z. phys. Chem., **46**, 602 (1903).

The increase of solubility with the temperature is much less in the case of silver chloride than of the other two salts. It is of some interest to apply to these results the integrated form of the van't Hoff equation:

$$\log_e \frac{S_2}{S_1} = \frac{L}{2R} \frac{T_2 - T_1}{T_1 T_2}$$

Since there are undoubtedly considerable errors in the very small solubility at 20° of the sulphocyanate and bromide, the best method is to use the formula in calculating this solubility (S_1) from that at 100° (S_2) with the help of the heat of solution (L). The values of the heat of precipitation as determined by Thomsen* at about 18° by metathesis, which are equal to the heat L absorbed by the dissolving of one equivalent, are 15,850 cal. for AgCl. 22,400 cal. for AgSCN, and 20,100 cal. for AgBr. The so calculated values of the solubility × 10^{-6} at 20° are: 8.1 for AgCl, 0.62 for AgSCN, and 0.47 for AgBr. The agreement with the observed values is as good as could be expected in the case of the last two salts, but is not very satisfactory in the case of silver chloride. It is possible, of course, that the assumption involved in the integration that the heat of solution remains constant through so wide a temperature-interval is attended with considerable error.

Attention may also be called to the relatively large solubility of silver chloride at 100°, which amounts to 21.8 milligrams per liter. This shows clearly that the statement made in several text-books on quantitative analysis† that this substance may be washed with hot water is a misleading one.

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*See Ostwald's Lehrbuch, II, 1, 335, 439.

†Classen, Ausgewählte Methoden der analytischen Chemie, **1**, 2; Fresenius, Anleitung zur quant. chem. Analyse (6te Aufl.) **1**, 298-299; Jannasch, Praktischer Leitfaden der Gewichtsanalyse, **1**, 10.

PART XI.

THE EQUIVALENT CONDUCTANCE OF THE HYDROGEN-ION DERIVED FROM TRANSFERENCE EXPERIMENTS WITH NITRIC ACID.

BY ARTHUR A. NOYES AND YOGORO KATO.

PART XI.

THE EQUIVALENT CONDUCTANCE OF HYDROGEN-ION DERIVED FROM TRANSFERENCE EXPERIMENTS WITH NITRIC ACID.

111. OUTLINE OF THE INVESTIGATION.

In an article published four years ago by A. A. Noyes and G. V. Sammet* there were described some transference determinations made with $\frac{1}{20}$, $\frac{1}{60}$ and $\frac{1}{80}$ normal hydrochloric acid at 10°, 20°, and 30°, which when combined with the equivalent conductance of chloride-ion (using the value of Kohlrausch) yielded for hydrogen-ion a much higher equivalent conductance than that which had been derived from the conductivity of acids at high dilutions. Thus the value for hydrogen-ion at 18° derived from the transference experiments was 330, while that of Kohlrausch derived from conductivity was 318. This serious divergence appeared greater than the possible errors in the transference determinations†; and it seemed as if it must be due either (1) to an error in the extrapolated values of the equivalent conductance of acids at zero concentration, (2) to the formation of complex-ions or some other abnormality of the hydrochloric acid, or (3) to a marked difference in the relative velocities of the hydrogen-ion and the anion, at moderate and at very low concentrations. To test the first of these possibilities a study of the effect of the impurities in the water upon the conductance of very dilute hydrochloric and nitric acids was made in this laboratory by H. M. Goodwin and R. Haskell,‡ the results of which showed that, after eliminating the effect of impurities as far as possible, a value for the equivalent conductance of hydrogen-ion at extreme dilution (315 at 18°) even lower than that previously derived by Kohlrausch (318) was obtained.

In view of these results it did not seen possible that the divergence could be due to the first-mentioned cause. The present investigation was therefore undertaken, in order to test the second explanation, or that being excluded, to establish the correctness of the third one.

For it was thought that independent transference experiments with another acid, if they yielded results concordant with those with hydrochloric acid, would serve both to exclude any specific error that might arise from complex-ion formation or other individual peculiarity of that

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*J. Am. Chem. Soc., **24**, 944-968; **25**, 165-168 (1902-3); Ztschr. phys. Chem., **43**, 49-74 (1903).

†The experimental results of Noyes and Sammet have recently been fully confirmed by those of Jahn, Joachim and Wolff (Z. phys. Chem., **58**, 641 (1907).

‡Phys. Rev., **19**, 369-396 (1904); Proc. Am. Acad., **40**, 399-415 (1904). Reviewed in Z. phys. Chem., **52**, 630 (1905).

acid and to confirm the experimental accuracy of the transference data, and that they would thus establish the fact that a marked change in the relative migration-velocity of the ions of acids takes place on passing to very low concentrations. Nitric acid was selected as the second acid, since it is of quite a different chemical character.* Another purpose of this investigation, bearing directly on the third suggestion mentioned above, was to extend the transference measurements with both acids to a dilution of about 0.002 normal.

112. PREPARATION AND STANDARDIZATION OF THE SOLUTIONS.

The chemically pure nitric acid of trade was freed from lower oxides of nitrogen by diluting it with two-thirds its volume of conductivity water and drawing a current of purified air through it. It was carefully tested (using 5–10 c.cm.) for chloride with silver nitrate, for sulphate by evaporation with barium chloride, for ammonia with Nessler reagent, and for nitrite by diluting and adding starch and potassium iodide. These impurities could not be detected at all, or were present only in entirely insignificant quantity. Diluter solutions (from 0.06 to 0.0006 normal) were made up with water having in all cases a specific conductance lying between 0.9 and 1.2×10^{-6} reciprocal ohms at 18°, and were titrated with the help of phenolphthalein against a 0.1 normal solution of barium hydroxide, which had been repeatedly crystallized and was proved to be substantially free from chloride, and also from silica, calcium, strontium, or other metals than barium (by precipitating with sulphuric acid and evaporating the filtrate to dryness in a platinum dish, when a scarcely weighable residue was obtained). The strength of the barium hydroxide solution was determined gravimetrically both by precipitating with sulphuric acid after neutralizing with hydrochloric acid and by evaporating to dryness with pure nitric acid and weighing the residue of $Ba(NO_3)_2$ after heating to 160° – 180°. The two methods gave for the content of the solution in milli-equivalents per kilogram $\left\{\begin{matrix}110.61\\110.58\end{matrix}\right\}$ and $\left\{\begin{matrix}110.74\\110.71\end{matrix}\right\}$ respectively; the value adopted was 110.64. Afterwards two other solutions of barium hydroxide were prepared and titrated against nitric acid solutions which had been standardized against the first barium hydroxide solution. Solution No. 2 contained 0.11904,† and solution No. 3 contained 0.05859‡ equivalents per kilogram of solution.

The five solutions of nitric acid varying from about 0.06 to 0.006

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*A single transference experiment has already been made with this acid at 25° at 0.05 normal concentration by Bein (Z. phys. Chem., **27**, 44. 1898).

†186.83 gm. of this solution (the total amount used in three concordant experiments) neutralized 388.08 gms. of HNO_3 Sol. No. 2.

‡118.19 gm. of this solution (used in five concordant experiments) neutralized 1048.90 gms. of HNO_3 Sol. No. 5.

normal, which were standardized for use in this work against these barium hydroxide solutions showed as a mean in each case of 5 or 6 determinations a content in milli-equivalents per kilogram of solution as follows:

	No. 1	No. 2	No. 3	No. 4	No. 5
Content	59.22	57.42	18.426	6.809	6.605
A. D.	0.01	0.00	0.003	0.001	0.001

The very dilute solutions (approximately 0.002 normal) of nitric and hydrochloric acids employed could hardly be titrated with sufficient accuracy by this method. The concentrations both of the original solutions and of the portions after electrolysis were therefore determined by measuring their conductance by the usual Kohlrausch method in a cylindrical cell with horizontal electrodes, and dividing the corresponding specific conductance by the equivalent conductance of the acid in question at this concentration and temperature. Goodwin and Haskell[*] have recently determined the equivalent conductances at 18° in 0.002 normal solution to be 371.3 for HNO_3, and 375.0 for HCl at 18°, from which follows with the help of Déguisne's temperature-coefficients:[†] 383.4 for HNO_3 and 387.4 for HCl at 20°, which are the values we have used in calculating the original concentrations. The actual conductance measured in the conductivity vessel, the specific conductance, and the concentration in milli-equivalents per liter calculated therefrom were as follows:

	Nitric acid solution		Hydrochloric acid solution	
	No. 6.	No. 7.	No. 1.	No. 2.
Actual conductance $\times 10^6$	2,142	,094	1,975	[*]2,136
Specific conductance $\times 10^6$	847.3	828.4	781.3	845.0
Milli-equivalents per liter	2.210	2.161	2.017	2.181

[*] The value found before the first experiment with this solution was 21855, that between the fourth and fifth experiments was 21372, showing that there was no considerable change from contamination during the course of the work.

The conductance-capacity of the conductivity vessel was 0.3956 for all the measurements presented in this article.[‡] Hydrochloric acid solution No. 1 was made by diluting quantitatively by weight (with water of conductivity 0.9×10^{-6}) a 0.13737 normal solution which had been standardized by weighing the silver chloride obtainable from it; the concentration calculated from the dilution was 2.015 in close agreement with that derived from the conductivity (2.017). Solution No. 2 was prepared from the same stock solution, which was itself made by treating pure salt with pure sulphuric acid, redistilling the strong acid obtained, and diluting it; it was proved to be free from non-volatile matter and from sulphuric acid.

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[*] Phys. Rev., **19**, 381, 383 (1904). These values like all of ours given below were not corrected for the conductance of the water.

[†] Kohlrausch and Holborn, Leitvermögen der Elektrolyte (1898), p. 199.

[‡] A 0.009954 normal potassium chloride solution measured in it showed as an average of several determinations a conductance of 3111.3×10^{-6} reciprocal ohms.

113. DESCRIPTION OF THE EXPERIMENTS.

The apparatus, consisting of two connecting **U**-tubes, was almost identical with that used by Noyes and Sammet, and the procedure followed in the transference experiments was nearly the same. Referring the reader therefore to their article* for the main features, we will here describe only the modifications adopted in our work. In order to avoid all danger from leakage, the two **U**-tubes were joined by drawing over their ends two thicknesses of light black tubing, tightly wiring this on, and entirely covering the joint with melted paraffin. The anode consisted of a circular platinum plate, convex downward, soldered with gold to a platinum wire. The cathode was a straight platinum wire which dipped into the solution always less than 1 cm., so that by having the current dense the reduction of the nitric acid was as far as possible prevented. Since the solution weakened around the cathode and concentrated around the anode, to avoid stirring, the cathode arm was filled with liquid nearly to the top, while the anode arm was filled only a few centimeters above the bend and the electrode was placed just below the surface. To keep the solution at this level the anode arm was fitted with a rubber stopper carrying a delivery tube which dipped into an outside vessel of water whose level could be varied.

Given in outline, the method of carrying out the transference experiments consisted in passing a suitable current for three hours and fifteen minutes (except when otherwise noted in the table) through the standard nitric or hydrochloric acid solutions in the apparatus just described, determining the quantity of electricity by means of two silver coulometers placed in series with it, one on either side, dividing the electrolyzed solution into a cathode, an anode, and three middle portions, and titrating each of these with barium hydroxide (or, in the case of the 0.002 normal solutions, measuring the conductance at 20°) to determine the concentration-changes. From the analyses of the cathode and anode portions two separate values of the transference-number were obtained, and by the analysis of the middle portions it was made certain that no error arose through convection.

The method of procedure at the end of the electrolysis was to transfer by means of a pipette the three middle portions to tared wide-mouth Erlenmeyer flasks with rubber stoppers. Then the two **U**-tubes were separated from each other, stoppered, well cleaned and dried outside, and weighed. The solutions in them were then, after thorough mixing, poured as completely as practicable into tared flasks, again weighed, and finally titrated, allowance being made in the calculation for the small portion that remained in the tubes, which were themselves cleaned, dried, and

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*J. Am. Chem. Soc., **24**, 946 (1902); Ztschr. phys. Chem., **43**, 51 (1903).

weighed empty. In the titration of all the portions, the quantity of barium hydroxide solution added was determined by again weighing the flasks containing them after exact neutralization with the base. In those cases where the titration was replaced by a measurement of the conductance, each portion was poured in succession into a cylindrical conductance-cell with horizontal platinized electrodes 2.5 cm. apart and measured as accurately as possible, using three resistances in the rheostat.

The principal error to be feared was that which might arise in the analysis of the cathode portion through the reduction of some of the nitric acid by the electrolytic hydrogen. To reduce this to a minimum the cathode was, as already stated, made as small as possible. Since careful analytical tests* showed (except in one experiment, No. 2, where the cathode was known to be badly arranged) no nitrite or ammonia in the cathode portion or nitrous vapors in the hydrogen evolved, there is good reason to believe that the error from this source was not serious in most of the other experiments. The effect of this error, it may be noted, would be to cause an apparent *increase* in the transference number of the anion when calculated from the cathode change.

In case of the 0.002 normal hydrochloric acid solution investigated there was the possibility of an opposite error from the liberation of chlorine at the anode, which would have resulted in too small a transference number as calculated from the anode change. With so very dilute a solution and the low current-density used, there was probably little danger of this; but to detect any such effect, two different forms of anodes were employed — a short platinum wire in experiments 1 – 5 (see table 122) and a platinum disc in experiments 6, 7, 9, and 10. As the mean results (167.8 and 168.8) with the two electrodes with such different surface-areas agreed almost completely, it seems hardly possible that there was a serious error from this source, especially in the latter experiments.†

In order to determine what error, if any, might arise in the very dilute solutions from contamination during the experiment, a "blank" experiment was made, in which the solution was treated in absolutely the same way as usual except that no current was passed. The stock solution of hydrochloric acid used (No. 2) had a conductance of 21372 and the portions withdrawn at the end of the experiment had conductances as follows: *K*,* 21336; M_K, 21355; *M*, 21349; M_A, 21349; *A*, 21356. There was on an average a decrease of 0.1 per cent. Although this would cause a not inconsiderable divergence of the cathode and anode transference numbers, yet it would not affect their mean appreciably; therefore no correction was made for it (except that the use of 21360 as the initial value eliminated it in great measure in the experiments with this solution.)

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*These tests were made by adding to 10 c.cm. of the cathode portion after its neutralization a few drops of pure sulphuric acid and some starch solution containing potassium iodide; by adding to 10 c.cm. of the neutralized portion a few drops of Nessler reagent; and by conducting the hydrogen evolved at the cathode through a tube containing filter paper moistened with a solution of starch and potassium iodide. All these tests gave a slight positive indication in the one experiment mentioned above, but in no other case, though they were tried in most of them.

†The cathodes were also varied in form (since the cathode results were considerably higher than the anode results), though there seemed to be no possibility of an abnormal reaction. A platinum disc was used in experiments 1-5, a spiral wire in 6-8, and a short straight wire in 9-10. The form of electrode had no influence, however. In experiment 8 a silver anode was used.

114. THE EXPERIMENTAL DATA.

The data of the experiments and the calculated transference values for the 0.06 — 0.007 normal nitric acid solutions are given in tables 132 – 134. The ***first*** column contains the number of the experiment; the ***second***, the number of the acid solution used; the ***third***, letters representing the different portions submitted to analysis, *K* signifying the cathode solution, M_K the adjoining middle portion, *M* the next portion, M_A the portion adjoining the anode, and *A* the anode portion itself; the ***fourth***, the weight in grams of the separate portions; the ***fifth*** contains the number of grams of barium hydroxide solution used in neutralizing the portions after the electrolysis; the ***sixth***, the initial content, expressed in equivalents and multiplied by 10^6, as calculated from the weight of the portion and the standardization value;† the ***seventh***, the final content calculated from the barium hydroxide used; the ***eighth***, the change in content of the separate portions; the ***ninth***, the total change in content, which includes the changes in the portions adjoining the cathode and anode;‡ the ***tenth***, the milligrams of silver precipitated in the coulometers; and the ***eleventh***, the calculated transference numbers for the anion multiplied by 1000.§

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*For the meaning of these letters see the next paragraph.

†See section 113, BaO_2H_2 Solution No. 1 was used in experiments 1 to 6; Solution No. 2 in experiments 7 to 26; and Solution No. 3 in experiments 27 to 32.

‡Except where the change in the adjoining portion was opposite in sign to that in the electrode portion.

§The way in which these were calculated may be illustrated with the help of the data obtained in the first experiment. The cathode portion submitted to analysis weighed 214.08 grams and was found to require 107.72 gm. of the BaO_2H_2 solution containing 0.11064 milli-equivalents per gram, so that the final content of the portion was the product of these last two quantities or 11.918 milli-equivalents. To determine the original content the weight of the portion is multiplied by the original concentration of the solution (0.05922 milli-equiv. per gm.), which gives 12.678 milli-equivalents. The decrease in content in the cathode portion is, therefore, 0.760 milli-equivalents. Adding to this the decrease in the adjoining middle portion (0.005) and dividing by the number of milli-equivalents of silver (523.0/107.93) precipitated in the coulometer, the transference number is found to be 0.1579. The small correction for the change in weight of the electrode portions by the electrolysis and transference is applied later.

Table 132.—*Transference data for* 0.058 *or* $\frac{1}{17}$ *normal nitric acid at* 20°.

Experiment No.	Solution No.	Portion.	Weight of portion.	BaO_2H_2 solution used.	Initial content.	Final content.	Change in content.	Total change in content.	Ag in coulometers.	Transference number $\times 10^3$.
1	2	3	4	5	6	7	8	9	10	11
1	1	K	214.08	107.72	12,678	11,918	— 760	— 765	523.2	157.9
		M_K	74.55	39.86	4,415	4,410	— 5	......	......	......
		M	212.29	113.50	12,575	12,558	— 17	......	......	......
		M_A	186.16	99.67	11,025	11,028	+ 3	......	......	......
		A	303.87	169.51	17,995	18,755	+ 760	+ 763	522.9	157.4
2	1	K	224.01	107.59	13,266	11,904	— 1,362	—1,375	919.5	161.4
		M_K	186.40	99.65	11,039	11,026	— 13	......	......	......
		M	185.02	99.01	10,957	10,955	— 2	......	......	......
		M_A	108.02	57.86	6,397	6,402	+ 5	......	......	......
		A	298.46	171.71	17,675	19,002	+ 1,327	+1,332	919.7	156.3
3	1	K	245.61	116.57	14,545	12,898	— 1,647	—1,686	1,129.5	161.1
		M_K	126.48	67.56	7,490	7,451	— 39	......	......	......
		M	163.15	87.31	9,662	9,660	— 2	......	......	......
		M_A	137.35	73.59	8,134	8,142	+ 8	......	......	......
		A	268.43	158.32	15,897	17,517	+ 1,620	+1,628	1,129.3	155.6
4	1	K	304.16	147.75	18,012	16,348	— 1,664	—1,664	1,118.6	160.6
		M_K	109.63	58.62	6,492	6,501	+ 9	......	......	......
		M	182.99	97.86	10,837	10,828	— 9	......	......	......
		M_A	155.70	83.48	9,221	9,231	+ 10	......	......	......
		A	273.97	161.19	16,224	17,834	+ 1,610	+1,620	1,118.8	156.3
5	1	M	281.68	137.57	16,681	15,221	— 1,460	—1,460	1,019.9	154.5
		M_K	134.58	72.08	7,970	7,975	+ 5	......	......	......
		M	134.20	71.83	7,947	7,947	± 0	......	......	......
		M_A	139.90	75.01	8,285	8,299	+ 14	......	......	......
		A	221.38	131.64	13,110	14,565	+ 1,455	+1,469	1,020.1	155.4
6	1	K	304.32	149.65	18,022	16,558	— 1,464	—1,464	1,012.8	156.0
		M_K	127.83	68.43	7,570	7,572	+ 2	......	......	......
		M	136.01	72.74	8,055	8,048	— 7	......	......	......
		M_A	132.70	71.50	7,859	7,911	+ 52	......	......	......
		A	244.75	143.75	14,494	15,906	+ 1,412	+1,464	1,012.9	156.0
7	2	K	267.30	122.93	15,349	13,601	— 1,748	—1,755	1,201.3	157.7
		M_K	128.27	66.50	7,365	7,358	— 7	......	......	......
		M	140.92	73.07	8,091	8,085	— 6	......	......	......
		M_A	131.81	68.51	7,568	7,580	+ 12	......	......	......
		A	236.68	138.33	13,590	15,305	+ 1,715	+1,727	1,201.2	155.2
8	2	K	256.11	120.13	14,705	13,292	— 1,413	—1,429	988.3	156.0
		M_K	148.68	77.01	8,537	8,521	— 16	......	......	......
		M	141.13	73.15	8,103	8,094	— 9	......	......	......
		M_A	132.89	69.05	7,630	7,640	+ 10	......	......	......
		A	274.66	155.27	15,770	17,180	+ 1,410	+1,420	989.4	155.0
9	2	K	295.01	141.78	16,939	15,687	— 1,252	—1,255	861.8	157.2
		M_K	105.16	54.54	6,038	6,035	— 3	......	......	......
		M	148.18	76.88	8,008	8,506	— 2	......	......	......
		M_A	147.77	76.75	8,485	8,492	+ 7	......	......	......
		A	281.13	157.05	16,144	17,376	+ 1,232	+1,239	861.4	155.2
10	2	K	258.40	124.30	14,837	13,753	— 1,084	—1,085	758.2	154.5
		M_K	135.90	70.51	7,803	7,802	— 1	......	......	......
		M	143.28	74.35	8,227	8,227	± 0	......	......	......
		M_A	139.93	72.63	8,034	8,036	+ 2	......	......	......
		A	253.26	141.29	14,542	15,633	+ 1,091	+1,093	757.6	155.7
11	2	K	343.52	167.97	19,725	18,584	— 1,141	—1,147	783.3	158.1
		M_K	148.88	77.20	8,548	8,542	— 6	......	......	......
		M	162.04	84.05	9,304	9,300	— 4	......	......	......
		M_A	139.38	72.33	8,003	8,003	± 0	......	......	......
		A	256.25	143.14	14,713	15,838	+ 1,125	+1,125	783.0	155.0

TABLE 132.—*Transference data for* 0.058 *or* $\frac{1}{17}$ *normal nitric acid at* 20°—Continued.

Experiment No.	Solution No.	Portion.	Weight of portion.	BaO_2H_2 solution used.	Initial content.	Final content.	Change in content.	Total change in content.	Ag in coulometers.	Transference number $\times 10^3$.
1	2	3	4	5	6	7	8	9	10	11
12	2	K	275.18	133.84	15,801	14,808	— 993	— 996	687.1	156.5
		M_K	154.33	80.06	8,861	8,858	— 3	......	......	......
		M	150.66	78.12	8,650	8,644	— 6	......	......	......
		M_A	132.84	68.94	7,627	7,628	+ 1	......	......	......
		A	304.76	167.07	17,499	18,485	+ 986	+ 987	686.8	155.1

TABLE 133.—*Transference data for* 0.0184 *or* $\frac{1}{54}$ *normal nitric acid at* 20°.

Experiment No.	Solution No.	Portion.	Weight of portion.	BaO_2H_2 solution used.	Initial content.	Final content.	Change in content.	Total change in content.	Ag in coulometers.	Transference number $\times 10^3$.
1	2	3	4	5	6	7	8	9	10	11
13	3	K	288.64	40.98	5,319	4,879	—440	—443	300.7	159.0
		M_K	142.34	22.01	2,623	2,620	— 3	......	......	......
		M	180.71	27.93	3,329	3,325	— 4	......	......	......
		M_A	150.21	23.24	2,767	2,767	0	......	......	......
		A	321.64	53.39	5,927	6,370	+443	+443	300.8	159.0
14	3	K	305.45	42.31	5,628	5,037	—591	—591	402.0	158.7
		M_K	151.88	23.51	2,799	2,799	0	......	......	......
		M	......	......	......	......	......	......	......	......
		M_A	129.16	20.01	2,380	2,382	+ 2	......	......	......
		A	308.11	52.70	5,677	6,273	+596	+598	401.8	160.6
15	3	K	334.04	46.44	6,155	5,529	—626	—630	420.8	161.6
		M_K	157.46	24.34	2,901	2,897	— 4	......	......	......
		M	164.29	25.42	3,027	3,026	— 1	......	......	......
		M_A	133.13	20.62	2,453	2,455	+ 2	......	......	......
		A	363.95	61.59	6,706	7,332	+626	+628	421.0	161.0
16	3	K	353.27	49.64	6,509	5,909	—600	—601	400.5	162.0
		M_K	161.93	25.06	2,984	2,983	— 1	......	......	......
		M	175.48	27.13	3,233	3,230	0	......	......	......
		M_A	136.96	21.23	2,524	2,527	+ 3	......	......	......
		A	299.07	51.23	5,511	6,099	+588	+591	400.5	159.2
17	3	K	342.27	46.04	6,307	5,481	—826	—833	564.6	159.2
		M_K	154.70	23.89	2,851	2,844	— 7	......	......	......
		M	171.63	26.57	3,162	3,163	+ 1	......	......	......
		M_A	145.82	22.60	2,687	2,690	+ 3	......	......	......
		A	347.01	60.64	6,394	7,219	+825	+828	564.7	158.3
18	3	K	280.38	36.50	5,166	4,345	—821	—822	552.8	160.5
		M_K	145.40	22.50	2,679	2,678	— 1	......	......	......
		M	159.65	24.70	2,941	2,940	— 1	......	......	......
		M_A	135.00	20.97	2,487	2,496	+ 9	......	......	......
		A	307.95	54.44	5,674	6,480	+806	+815	553.0	159.1
19	3	K	340.61	45.45	6,276	5,410	—866	—870	588.7	159.5
		M_K	127.96	19.77	2,358	2,354	— 4	......	......	......
		M	159.91	24.74	2,947	2,945	— 2	......	......	......
		M_K	152.38	23.65	2,808	2,815	+ 7	......	......	......
		A	355.91	62.33	6,558	7,419	+861	+868	588.8	159.1
20	3	K	287.80	39.08	5,303	4,653	—650	—656	441.8	160.3
		M_K	102.36	15.79	1,886	1,880	— 6	......	......	......
		M	111.64	17.26	2,057	2,055	— 2	......	......	......
		M_A	131.39	20.30	2,421	2,417	— 4	......	......	......
		A	423.23	70.95	7,799	8,446	+647	+647	441.7	158.1

TABLE 134.—*Transference data for* 0.0067 *or* $\frac{1}{150}$ *normal nitric acid at* 20°.

Experiment No.	Solution No.	Portion.	Weight of portion.	BaO_2H_2 solution used.	Initial content.	Final content.	Change in content.	Total change in content.	Ag in coulometers.	Transference number × 10³.
1	2	3	4	5	6	7	8	9	10	11
21	4	K	......	......	......	......	......	......	636.4	......
		M_K	129.36	7.02	881	836	— 45	......	......	......
		M	159.75	8.84	1,087	1,052	— 35	......	......	......
		M_A	132.01	7.65	899	911	+ 12	......	......	......
		A	372.55	29.12	2,537	3,467	+930	+942	636.5	159.8
22	4	K	370.41	14.24	2,522	1,696	—827	—850	578.4	158.6
		M_K	135.75	7.57	924	901	— 23	......	......	......
		M	162.43	9.14	1,106	1,088	— 18	......	......	......
		M_A	124.36	7.20	847	857	+ 10	......	......	......
		A	379.59	28.75	2,584	3,422	+838	+848	578.5	158.2
23	4	K	383.23	17.51	2,609	2,085	—524	—531	352.9	160.3
		M_K	123.40	7.00	840	833	— 7	......	......	......
		M	142.82	8.09	972	963	— 9	......	......	......
		M_A	113.52	6.54	771	778	+ 7	......	......	......
		A	406.87	27.60	2,770	3,285	+515	+522	352.7	159.5
24	4	K	339.32	15.20	2,311	1,810	—501	—507	337.3	162.2
		M_K	123.67	7.02	842	836	— 6	......	......	......
		M	162.28	9.26	1,105	1,102	— 3	......	......	......
		M_A	111.23	6.38	757	759	+ 2	......	......	......
		A	376.62	25.71	2,564	3,061	+497	+499	337.4	159.6
25	4	K	352.55	16.62	2,401	1,978	—423	—429	281.7	164.3
		M_K	133.83	7.60	911	905	— 6	......	......	......
		M	140.73	8.00	958	952	— 6	......	......	......
		M_A	127.78	7.33	870	873	+ 3	......	......	......
		A	359.34	24.03	2,447	2,860	+413	+416	282.0	159.3
26	5	K	348.65	14.68	2,303	1,747	—556	—559	377.5	159.7
		M_K	139.89	7.73	924	921	— 3	......	......	......
		M	139.52	7.67	922	913	— 9	......	......	......
		M_A	115.36	6.43	762	766	+ 4	......	......	......
		A	393.06	26.49	2,596	3,153	+557	+561	378.0	160.3
27	5	K	391.96	35.02	2,589	2,051	—538	—546	353.7	166.7
		M_K	133.43	14.90	881	873	— 8	......	......	......
		M	167.47	18.77	1,106	1,100	— 6	......	......	......
		M_A	132.85	14.99	877	878	+ 1	......	......	......
		A	419.49	56.11	2,771	3,288	+517	+518	353.5	158.1
28	5	K	369.56	31.75	2,444	1,861	—583	—593	397.3	161.1
		M_K	136.30	15.19	900	890	— 10	......	......	......
		M	148.75	16.68	983	978	— 5	......	......	......
		M_A	116.62	13.27	770	777	+ 7	......	......	......
		A	394.42	54.39	2,605	3,187	+582	+589	397.5	160.0
29	5	K	407.05	36.61	2,688	2,145	—543	—550	371.2	159.9
		M_K	128.28	14.34	847	840	— 7	......	......	......
		M	148.07	16.62	978	974	— 4	......	......	......
		M_A	129.11	14.64	853	858	+ 5	......	......	......
		A	416.34	56.22	2,750	3,294	+544	+549	371.2	159.6
*30	5	K	407.80	39.75	2,693	2,329	—364	—368	236.2	168.2
		M_K	112.65	12.64	744	740	— 4	......	......	......
		M	160.22	18.07	1,058	1,059	+ 1	......	......	......
		M_A	119.82	13.49	791	791	+ 0	......	......	......
		A	412.34	52.52	2,724	3,078	+354	+354	236.2	161.8

*In this Experiment (No. 30) the period during which the solution was electrolyzed was greater than the usual time (3¼ hours), namely, 6 hours.

TABLE 134.—*Transference data for* 0.0067 *or* $\frac{1}{150}$ *normal nitric acid at* 20°—Continued.

Experiment No.	Solution No.	Portion.	Weight of solution.	BaO_2H_2 solution used.	Initial content.	Final content.	Change in content.	Total change in content.	Ag in coulometers.	Transference number $\times 10^3$.
1	2	3	4	5	6	7	8	9	10	11
*31	5	K	286.25	36.52	2,551	2,140	—411	—417	275.6	163.3
		M_K	143.83	16.11	950	944	— 6	......	......	......
		M	148.08	16.59	978	972	— 6	......	......	......
		M_A	107.04	12.07	707	707	0	......	......	......
		A	382.47	49.94	2,526	2,926	+400	+400	275.8	156.6
*32	5	K	409.57	34.24	2,705	2,006	—699	—703	472.0	160.7
		M_K	119.64	13.41	790	786	— 4	......	......	......
		M	164.62	18.49	1,087	1,083	— 4	......	......	......
		M_A	131.90	14.96	871	877	+ 6	......	......	......
		A	410.17	58.11	2,709	3,404	+695	+701	472.1	160.3

*In these experiments (Nos. 31 and 32) the solution was electrolyzed 4¼ hours and 6 hours, respectively.

TABLE 135.—*Transference data for* 0.0022 *normal nitric acid at* 20°.

Experiment No.	Solution No.	Portion.	Weight of portion.	Actual conductance $\times 10^6$.	Change in conductance $\times 10^6$.	Change in content.	Total change in content.	Ag in coulometers.	Transference number $\times 10^3$.
1	2	3	4	5	6	7	8	9	10
*33	6	K	349.79	1,498	—644	—2,336	—2,345	154.5	163.8
		M_K	97.13	2,133	— 9	— 9	......	......	......
		M	151.75	2,139	— 3	— 5	......	......	......
		M_A	118.86	2,156	+ 14	+ 17	......	......	......
		A	389.53	2,707	+565	+2,282	+2,299	154.5	160.6
34	7	K	349.70	1,813	—281	—1,019	—1,021	66.8	165.1
		M_K	119.33	2,092	— 2	— 2	......	......	......
		M	......	2,086	— 8	......	......	......	......
		M_A	123.57	2,095	+ 1	+ 1	......	......	......
		A	359.49	2,358	+264	+ 984	+ 985	66.7	159.3
35	7	K	359.94	1,562	—532	—1,986	—1,988	131.3	......
		M_K	106.04	2,092	— 2	— 2	......	......	......
		M	134.48	2,089	— 5	— 7	......	......	......
		M_A	113.76	2,104	+ 10	+ 12	......	......	......
		A	393.43	2,571	+477	+1,946	+1,958	131.2	161.0
36	7	K	350.57	1,528	—566	—2,058	—2,073	135.5	165.1
		M_K	104.87	2,080	— 14	— 15	......	......	......
		M	132.59	2,090	— 4	— 5	......	......	......
		M_A	115.59	2,105	+ 11	+ 13	......	......	......
		A	386.20	2,603	+509	+2,039	+2,052	135.5	163.4
37	7	K	......	......	......	......	......	134.6	......
		M_K	125.23	2,086	— 8	— 10	......	......	......
		M	134.42	2,095	+ 1	+ 1	......	......	......
		M_A	139.43	2,104	+ 10	+ 14	......	......	......
		A	376.86	2,606	+512	+2,001	+2,015	134.6	161.6

*In this experiment (No. 33) the electrolysis was continued for $4^1/_3$ hours instead of for 3¼ hours as usual.

Tables 135 and 136 present the results obtained with the more dilute solutions where the concentration was determined by conductance measurements. The first four columns are the same as in the preceding tables.

Table 136.—*Transference data for* 0.0021 *normal hydrochloric acid at* 20°.

Experiment No.	Solution No.	Portion.	Weight of portion.	Actual conductance $\times 10^0$.	Change in conductance $\times 10^6$.	Change in content.	Total change in content.	Ag in coulometers.	Transference number $\times 10^3$.
1	2	3	4	5	6	7	8	9	10
1	1	K	384.26	1,250	—725	—2,862	—2,883	178.6	174.2
		M_K	125.64	1,959	— 16	— 21	......	......	......
		M	135.42	1,971	— 4	— 5	......	......	......
		M_A	126.10	2,000	+ 25	+ 32	......	......	......
		A	389.93	2,658	+683	+2,736	+2,768	178.9	167.1
2	1	K	313.49	1,360	—615	—1,980	—1,988	123.9	173.3
		M_K	132.60	1,969	— 6	— 8	......	......	......
		M	131.29	1,973	— 2	— 3	......	......	......
		M_A	112.29	1,989	+ 14	+ 16	......	......	......
		A	385.67	2,455	+480	+1,902	+1,918	123.9	167.2
3	1	K	372.66	1,466	—509	—1,949	—1,955	120.2	175.8
		M_K	121.26	1,970	— 5	— 6	......	......	......
		M	135.37	1,970	— 5	— 7	......	......	......
		M_A	130.33	1,985	+ 10	+ 13	......	119.8	......
4	1	K	385.12	1,295	—680	—2,690	—2,738	171.0	173.0
		M_K	115.65	1,935	— 40	— 48	......	......	......
		M	143.10	1,959	— 16	— 23	......	......	......
		M_A	126.67	1,995	+ 20	+ 26	......	......	......
		A	430.37	2,577	+602	+2,661	+2,687	170.9	169.7
*5	1	K	388.28	1,497	—478	—1,906	—1,917	115.0	180.1
		M_K	122.78	1,966	— 9	— 11	......	......	......
		M	138.55	1,970	— 5	— 7	......	......	......
		M_A	122.73	1,975	+ 0	+ 0	......	......	......
		A	424.00	2,383	+408	+1,777	+1,777	114.8	167.0
6	2	K	420.70	1,546	—590	—2,549	—2,574	161.0	172.5
		M_K	121.58	2,116	— 20	— 25	......	......	......
		M	148.97	2,127	— 9	— 14	......	......	......
		M_A	102.76	2,163	+ 27	+ 28	......	......	......
		A	458.17	2,664	+528	+2,485	+2,513	161.1	168.5
*7	2	K	443.00	1,761	—375	—1,706	—1,710	105.8	174.4
		M_K	122.55	2,133	— 3	— 4	......	......	......
		M	143.52	2,136	+ 0	+ 0	......	......	......
		M_A	127.24	2,141	+ 5	+ 7	......	......	......
		A	476.09	2,473	+337	+1,648	+1,655	105.8	168.8
*8	2	K	436.04	1,862	—274	—1,227	—1,238	78.0	171.6
		M_K	107.32	2,126	— 10	— 11	......	......	......
		M	142.92	2,129	— 7	— 10	......	......	......
		M_A	118.21	2,078	— 58	— 70	......	77.7	......
9	2	K	458.82	1,819	—317	—1,494	—1,495	92.7	174.1
		M_K	107.75	2,135	— 1	— 1	......	......	......
		M	160.12	2,133	— 3	— 5	......	......	......
		M_A	104.29	2,142	+ 6	+ 6	......	......	......
		A	478.33	2,430	+294	+1,444	+1,450	92.8	168.8
10	2	K	438.20	1,835	—301	—1,355	—1,361	85.0	173.0
		M_K	114.76	2,131	— 5	— 6	......	......	......
		M	143.57	2,132	— 4	— 6	......	......	......
		M_A	104.46	2,136	+ 0	+ 0	......	......	......
		A	471.81	2,411	+275	+1,333	+1,333	84.9	169.3

*In experiments 5, 7, and 8 the electrolysis was continued for only 2¼ hours.

The *fifth* contains the actual conductance $\times 10^6$; the *sixth*, the difference between this value and the initial conductance $\times 10^6$ as given at the end of section 112;* the *seventh*, the corresponding change in content of the whole portion, expressed in 10^{-7} equivalents, obtained by multiplying this difference by the conductance-capacity of the vessel (0.3956), dividing by the equivalent conductance values 382.1 for HNO_3 and 385.8 for HCl,† and multiplying by the volume of the portion (obtained from its weight by multiplying it by 1.0018); and the *eighth*, the total change of content or the sum of the changes in the electrode portion and the adjoining portion. The *ninth* column contains the milligrams of silver deposited in the coulometers; and the *tenth*, the transference number for the anion $\times 10^3$.

115. SUMMARY OF THE TRANSFERENCE NUMBERS.

The following table contains a summary of the transference numbers derived from the preceding experiments together with the means derived therefrom. In finding the separate means of the cathode and anode values a few abnormally high or low values (designated by an asterisk) have been omitted.‡ To these means in the case of the two most concentrated solutions a correction has been applied to remove a small error introduced by the method used for the calculation of the separate values,§ and the results are designated "corrected means." These cathode and anode means have then been combined in the case of the three stronger nitric acid solutions under the assumption that each has a weight inversely proportional to the square of its average deviation (A. D.). Since the cathode values show in all three cases much greater variations, this procedure gives to the anode values a much greater weight, which would be *a priori* desirable since they are not subject to the possible error arising from the reduction of the nitric acid around the cathode. It is in fact very probable that both the larger variations and the greater magnitude of the cathode values are due to this cause. In spite of this source of error it is to be noted that the mean cathode value exceeds the mean anode value by only 0.9, 0.6, and 1.1 per cent, respectively, in the case of the three more concentrated solutions. Taking into account the fact that almost all other errors affect the two results in opposite directions we believe the final A. D. values give a fair measure of the probable precision of the final results, which is from 0.2 to 0.3 per cent for the 0.06 to 0.007 normal nitric acid solutions.

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*These initial values are: 2142 for HNO_3 Solution No. 6; 2094 for HNO_3 Solution No. 7; 1975 for HCl Solution No. 1, and 2136 for HCl Solution No. 2.

†These values are those of $d\underline{L}/dC$ at 0.002 normal, where $\underline{L}$ represents the specific conductance and C the equivalent concentration. We derived them through a careful consideration of all the results obtained by Goodwin and Haskell with both acids at 18° between the concentrations of 0.001 and 0.005 normal. The values were first derived at 18° and were found to be 370.0 for HNO_3 and 373.5 for HCl, and these were then increased with the help of Déguisne's coefficients so as to make them correspond to 20°. It is scarcely possible that the errors in these values exceed 0.3 per cent.

‡The high cathode values in experiments 2, 3, and 4 were probably due to reduction by the electrolytic hydrogen, which was proved to have taken place in experiment 2. The cathode value in experiment 22 was omitted since the middle portion showed a large change in content.

§Namely, in calculating the original content the total weight of the electrode portion was simply multiplied by the initial content per gram. That weight had, however, been increased, over what it would have been originally, at the anode by the weight of the transferred nitric acid and had been decreased by the electrolysis out

In the case of the 0.002 normal solutions of both acids the divergence of the cathode and anode mean values is much greater, and it seemed best to assign an equal weight to each without reference to the value of its average deviation; for the divergence probably arises in the main from a slight contamination of these very dilute solutions during the experiment, which would affect the cathode and anode values oppositely and about equally. The final A. D. values, which expressed as percentages are 0.7 per cent for the nitric acid and 1.0 per cent for the hydrochloric acid, are again a fair measure of the maximum error of which there is any reasonable probability.

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of it of the water corresponding to the hydrogen and oxygen evolved; and at the cathode it had been decreased by the weight of the transferred nitric acid.

By considering the effect of this on the result, it will readily be seen that when any acid of equivalent weight A, transference number n, and original content c in equivalents per gram of solution is electrolyzed as in this case with the production of hydrogen and oxygen, and the calculation is made as above (multiplying the total weight of the portion by c) then the anode transference-number should be increased by the fractional amount $(An - 9)c/n$ and the cathode transference number should be increased by the fractional amount Ac. In this case, with the strongest (0.058) normal solution, the corrections, applied (since $A = 63$, $n = 0.156$, and $c = 0.000058$) are $+0.03$ per cent on the anode value and $+0.36$ per cent on the cathode value. With the 0.0184 normal solutions the corrections are one-third of these percentages.

The corresponding correction was not applied by Noyes and Sammet to their results with hydrochloric acid. It would have the effect of increasing their final value at 0.05 normal (165.69) by just 0.17 per cent (to 165.96), while at the lower concentrations the correction would be scarcely appreciable.

A more simple way of calculating transference numbers from the experimental data is to refer the initial content to the weight of water present instead of to that of the whole solution, and to calculate correspondingly the weight of water in the portion after the electrolysis by subtracting from its total weight the weight of solute found in it; but even then a correction must be applied to the anode portion for the water electrolyzed out of it. The present basis of all such transference determinations is of course the assumption that the water itself does not migrate.

TABLE 137.—*Summary of the transference values.*

0.058 Normal HNO$_3$ at 20°.		
Experiment No.	Cathode.	Anode.
1	157.9	*157.4
2	*161.4	156.3
3	*161.1	155.6
4	*160.6	156.3
5	154.5	155.4
6	156.0	156.0
7	157.7	155.2
8	156.0	155.0
9	157.2	155.2
10	154.5	155.7
11	158.1	155.0
12	156.5	155.1
Mean	156.49	155.53
Corrected mean	157.05	155.58
a. d.	1.10	0.41
A. D.	0.36	0.12
Final mean	155.73	
Final A. D.	0.27	

0.0184 Normal HNO$_3$ at 20°.		
Experiment No.	Cathode.	Anode.
13	159.0	159.0
14	158.7	160.6
15	161.6	161.0
16	162.0	159.2
17	159.2	158.3
18	160.5	159.1
19	159.5	159.1
20	160.3	158.1
Mean	160.10	159.30
Corrected mean	160.29	159.32
a. d.	1.00	0.71
A. D.	0.35	0.25
Final mean	159.64	
Final A. D.	0.34	

0.0067 Normal HNO$_3$ at 20°.		
Experiment No.	Cathode.	Adode.
21	......	159.8
22	*158.6	158.2
23	160.3	159.5
24	162.2	159.6
25	164.3	159.3
26	159.7	160.3
27	*166.7	158.1
28	161.1	160.0
29	159.9	159.6
30	*168.2	161.8
31	163.3	*156.6
32	160.7	160.3
Mean	161.44	159.68
a. d.	1.36	0.69
A. D.	0.48	0.21
Final mean	149.96	
Final A. D.	0.44	

0.0022 Normal HNO$_3$ at 20°.		
Experiment No.	Cathode.	Anode.
33	163.8	160.6
34	165.1	159.3
35	163.5	161.0
36	165.1	163.3
37	......	161.6
Mean	164.4	161.2
a. d.	0.7	1.0
A. D.	0.4	0.5
Final mean	162.8	
Final A. D.	1.2	

0.0021 Normal HCl at 20°.		
Experiment No.	Cathode.	Anode.
1	174.2	*167.1
2	173.3	*167.2
3	175.8	......
4	173.0	*169.7
5	*180.1	*167.0
6	172.5	168.5
7	174.4	168.8
8	171.6	......
9	174.1	168.8
10	173.0	169.3
Mean	173.5	†168.8
A. D.	0.3	0.1
Final mean	171.1	
Final A. D.	1.7	

†The mean of all the anode values is 168.3 but it seems best to omit the first four, in which experiments an anode of small surface was used, and which are somewhat lower perhaps owing to the evolution of a small quantity of chlorine.

116. SUMMARY AND DISCUSSION.

The final results of the transference experiments described in this article, as well as of those carried out by Noyes and Sammet* with 0.05 — 0.006 normal hydrochloric acid at 20°,† are brought together in table 138. In this table are also given the values of the equivalent conductance of

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*Ztschr. phys. Chem., **43**, 63 (1903) ; J. Am. Chem. Soc., **24**, 958; **25**, 167 (1902-3).

†Corrected for the inaccuracy in their calculation as described in a preceding footnote.

hydrogen-ion calculated from each transference number and from the most probable values for nitrate-ion and chloride-ion (64.6 and 68.5, respectively) at 20° and extreme dilution.* In the last row of the table are given the corresponding values for zero concentration as derived from Goodwin and Haskell's conductivity experiments.†

TABLE 138.—*Final values of the transference-numbers and the equivalent conductance of hydrogen-ion.*

Equivalents per liter.		Transference-number $\times 10^3$.		Equivalent conductance of hydrogen-ion from experiments with	
HNO_3.	HCl.	HNO_3.	HCl.	HNO_3.	HCl.
0.058	0.051	155.7	166.0	350.3	344.2
0.0184	0.017	159.6	167.5	340.2	340.5
0.0067	0.0056	160.0	167.1	339.1	341.4
0.0022	0.0021	162.8	171.1	332.2	331.8
0	0	166.0	174.5	324.6	324.0

It will be seen from table 138 that, except at the highest concentration (0.055 normal), there is substantial agreement between the values of the equivalent conductance of the hydrogen-ion derived from the independent transference experiments with the two different acids, and that the (nearly constant) value for the concentration-interval between 0.018 and 0.006 normal is nearly 5 per cent larger than that derived from conductivity measurements at extreme dilution. The reality of this divergence, first discovered by Noyes and Sammet, confirmed as it is on the conductivity side by the investigation of Goodwin and Haskell and on the transference side by the recent determinations of Jahn, Joachim, and Wolff, and by these new experiments with nitric acid, can, we believe, no longer reasonably be doubted. It must therefore be concluded that *the transference number of the anion of acids, and therefore the ratio of the velocity of the anions to that of the hydrogen-ion, is several per cent larger at very small concentration* (0.001 normal and less) *than at moderate concentrations* (0.05 to 0.005 normal). Thus a change in the relative velocities takes place even after the concentration of the solute has become so small that as a medium the solution scarcely differs from the pure solvent. The fact that higher transference numbers were obtained with the 0.002 normal solutions than with the more concentrated solutions of both acids confirms the conclusion drawn from the comparison with the conductivity data. The values obtained at 0.002 normal show, moreover, that even at this very low concentration the velocities have not yet become identical with those at zero concentration.

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*The value here given for the Cl is that derived by Noyes and Sammet from Kohlrausch's conductivity data and the existing transference data for potassium chloride. That for the NO_3 ion we have obtained by subtracting from that for the Cl the difference for these two ions at 20° given by Kohlrausch (Sitzungsber. königl. preuss. Akad. der Wissensch., 1901, 1031). These values have then simply been multiplied by $(1-n)/n$.

†These investigators found for Λ_0 at 18° 377.0 for HNO_3 and 380.1 for HCl. The corresponding values at 20° calculated with Déguisne's coefficients are 389.2 and 392.5 respectively. Subtracting from these the values for the NO_3 and Cl ions (64.6 and 68.5) one obtains the values for the hydrogen ion given in the table.

This change of the transference number may, of course, arise either from an acceleration of the anion or from a retardation of the hydrogen-ion at very high dilution, or from both causes combined. The facts that salts do not as a rule show any change in their transference numbers after a moderate dilution is reached and that their ionization-values calculated from freezing-point lowering and other molecular properties agree with those corresponding to the conductance ratio (Δ/Δ_0)* make it probable, however, that it is the fast-moving hydrogen-ion that is mainly, if not wholly, affected.† It is under this (possibly incorrect) assumption, namely, that neutral ions have the same velocity at moderate and at very low concentrations, that the values, given in table 138, of the equivalent conductance of hydrogen-ion at various concentrations were derived.

The fact that the values of the equivalent conductance of hydrogen-ion are nearly constant for the interval of concentration 0.006 – 0.018 seems to indicate that these are the normal ones, and that the variations at lower concentrations arise from some secondary effect of a general character, determined perhaps by the smallness of the ion-concentration itself.

The results obtained at the highest concentration (0.05 to 0.06 normal) differ in the case of the two acids, which makes it seem probable that the variation in the stronger solution is due to some different cause, probably one of a specific chemical nature, from that which gives rise to the change at high dilutions.

As to the bearing of these results on the calculation of ionization-values, it may be said that in the case of largely ionized acids at moderate concentrations it seems in the light of now existing knowledge most appropriate to divide the observed equivalent conductance of the acid by a Λ_0 value obtained by adding to the equivalent conductance of the anion that for the hydrogen-ion obtained by the transference experiments above described at the concentration in question. On the other hand in the case of any acid solution in which the *ion*-concentration is less than 0.001 normal the older value (324 at 20° or 315 at 18°) for hydrogen-ion is to be preferred.

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*See A. A. Noyes, Z. phys. Chem., **52**, 634.

†It is therefore probable that the decrease in the conductance of strong acids always observed at very high dilutions is not wholly due to impurities in the water.

It is of interest to compare the ionization of hydrochloric acid computed in the manner just stated with that of neutral salts of the same ionic type, like potassium and sodium chlorides. At the concentration 0.05 normal the ionization-value derived from Kohlrausch's value (360) of the equivalent conductance of the acid at 18° is found to be 0.948, provided the equivalent conductance of hydrogen-ion is taken at 315 as derived from the conductivity of the acid at small concentrations; but it becomes 0.900 when the equivalent conductance of hydrogen-ion is taken 6.2 per cent larger than this, in accordance with the transference results. At this same concentration the ionization-values for potassium chloride and sodium chloride, as derived from their equivalent conductances, are 0.891 and 0.878. The approximate agreement of these values with the new one for hydrochloric acid seems to justify the extension to largely ionized acids of the principle that salts of the same ionic type have at the same concentration roughly the same degree of ionization.

PART XII.

GENERAL SUMMARY OF THE RESULTS.

BY ARTHUR A. NOYES.

PART XII.

GENERAL SUMMARY OF THE RESULTS.

It seems desirable at the close of this extended series of papers to summarize the more important results which have been attained, both in order to make them more readily available to readers who may not be interested in the details of the experiments, and in order to show more clearly, by bringing together all the more significant results, the general conclusions which can be drawn from them.

In order to carry out these investigations a new form of conductance vessel capable of withstanding high pressures and not liable to contaminate dilute aqueous solutions even at high temperatures had to be constructed at the start. The vessel or "bomb" which was developed as a result of several years' experimenting and which has been used successfully with only minor modifications for all the measurements above presented will be readily understood in its essential features by reference to figure 1 on page 10, and from the following brief description:

It consists of a cylindrical vessel *A* of about 125 c.cm. capacity provided with a cover *B* which is held in place by means of a large nut *C*, all these parts being made of steel. The bomb is lined throughout with sheet platinum. The cover is made tight by a small packing-ring of pure gold wire which fits into a small V-shaped groove. The body of the bomb serves as one electrode. The other electrode is brought in through the bottom of the bomb, being insulated inside by a piece of quartz and outside by mica layers *M*. The quartz-piece *Q* is in the form of a cylindrical cup about 2 cm. in external diameter and 2.7 cm. in height, the bottom of it being covered on the inside by the circular platinum-covered top of the electrode, which was usually well coated with platinum black. In the cover is a narrow cylindrical chamber provided with an auxiliary insulated electrode T_2, which serves to show the height of the liquid in the chamber and indirectly the volume of the liquid in the bomb. The cover also contains a small platinum tube T_1 through which the air may be exhausted from the bomb.

In most of the experiments made with the more dilute solutions, the bomb was modified, so as to reduce contamination, by removing the cup and flat electrode within it, and replacing these by a cylindrical platinum-iridium electrode usually about 10 mm. high and 7.2 mm. in diameter, which was supported on a vertical quartz cylinder, through the center of which the electrode rod passed downwards (see fig. 13, page 63).

For the measurements at 18° and 100° and in some of those at 128° and 156° the bomb was immersed in a liquid xylene or pseudocumene bath, but at the higher temperatures it was heated in the apparatus shown in fig. 2, page 12, in the vapors of boiling liquids (brombenzene at 156°, naphthalene at 218°, isoamylbenzoate at 260°, bromnaphthalene at 281°, and benzophenone at 306°). In the later experiments the heater and the electrical connections were so arranged that the bomb could be rotated (see fig. 14, page 64), thus causing thorough stirring of the contents.

By means of this apparatus conductance measurements have been made up to 306° at all or nearly all the temperatures just mentioned with sodium chloride, potassium chloride, silver nitrate, potassium sulphate, barium nitrate, hydrochloric acid, nitric acid, sulphuric acid, acetic acid, ammonium hydroxide, ammonium chloride, sodium acetate, and ammonium acetate; at the temperatures up to 218° with magnesium sulphate, and sodium hydroxide; and from 18° to 156° at intervals of 25° or 28° with nitric acid, phosphoric acid, sulphuric acid, potassium hydrogen sulphate, and barium hydroxide. With most of these substances the measurements have been made at four or more different concentrations varying between 0.1 and 0.002 normal.

The final values of the equivalent conductance of these substances will be found in the tables of the preceding parts on the following pages:

Potassium and sodium chlorides	47
Silver nitrate, barium nitrate, potassium sulphate, magnesium sulphate	103
Acetic acid and sodium acetate	137-8, 225
Ammonium hydroxide and ammonium chloride	174, 225
Hydrochloric acid	137, 262
Sodium hydroxide	174
Nitric acid, phosphoric acid, sulphuric acid, potassium hydrogen sulphate, and barium hydroxide	262

These conductivity results have interest from a theoretical standpoint mainly in two respects — first, with reference to the equivalent conductance of the ions or their specific migration-velocities; and second, with reference to the degree of ionization of the various substances.

The values at the different temperatures of the equivalent conductance (Λ_0) extrapolated for zero concentration or complete ionization were obtained with the help of a function of the form $\frac{1}{\Lambda_0} = \frac{1}{\Lambda} - K_1(C\Lambda)^{n-1}$, which corresponds to the equation $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$, by plotting $1/\Lambda$ against $(C\Lambda)^{n-1}$, varying the value of n till a linear plot was obtained, and then extrapolating for zero concentrations.* All the so-derived values of Λ_0 for the largely ionized electrolytes are summarized in the following table. The substances are arranged primarily according to the ionic type and secondarily in the order in which the Λ_0 values at 18° increase. In adjoining columns are given also the mean temperature-coefficient $\Delta\Lambda_0/\Delta t$ for the successive temperature-intervals and the ratio $\Lambda_{0(S)}/\Lambda_{0(KCl)}$ of the equivalent conductance of the substance in question to that of potassium chloride at the same temperature.

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*A discussion of this method of deriving the Λ_0-value will be found in section 17 (Part II, page 50).

TABLE 139.—*Equivalent conductance at zero concentration.*

Temperature.	Sodium acetate.			Sodium chloride.			Silver nitrate.		
	Λ_0	$\frac{\Delta\Lambda_0}{\Delta t}$	$\frac{\Lambda_0(S)}{\Lambda_0(KCl)}$	Λ_0	$\frac{\Delta\Lambda_0}{\Delta t}$	$\frac{\Lambda_0(S)}{\Lambda_0(KCl)}$	Λ_0	$\frac{\Delta\Lambda_0}{\Delta t}$	$\frac{\Lambda_0(S)}{\Lambda_0(KCl)}$
18	78.1		0.60	109.0		0.84	115.8		0.89
		2.53			3.09			3.06	
100	285		0.69	362		0.87	367		0.89
		2.95			3.44			3.62	
156	450		0.72	555		0.89	570		0.91
		3.40			3.31			3.39	
218	660		0.80	760		0.92	780		0.95
					3.33			2.94	
281	....	3.00	....	970		0.96	965		0.96
					4.40			4.00	
306	924		0.82	1080		0.96	1065		0.95
	Potassium chloride.			Ammonium chloride.			Sodium hydroxide.		
18	130.1		....	130.7		1.01	216.5		1.67
		3.46			3.47			4.60	
100	414		....	415		1.00	594		1.43
		3.77			3.80			4.30	
156	625		....	628		1.00	835		1.33
		3.23			3.43			3.63	
218	825		....	841		1.02	1060		1.29
		2.86			....			....	
281	1005		....	....	3.81	....	....		....
		4.60							
306	1120		....	1176		1.05		....	....
	Barium nitrate.			Potassium sulphate.			Barium hydroxide.		
18	116.9		0.90	132.8		1.02	222		1.71
		3.27			3.93			5.16	
100	385		0.93	455		1.10	645		1.56
		3.84			4.64			3.58	
156	600		0.96	715		1.14	847		1.36
		3.87			5.64			....	
218	840		1.02	1065		1.29	....		....
		4.44			6.27			....	
281	1120		1.11	1460		1.45	....		....
		7.20			10.6			....	
306	1300		1.16	1725		1.54	....		....
	Phosphoric acid.			Nitric acid.			Hydrochloric acid.		
18	338		2.60	377		2.90	379		2.91
		4.78			5.61			5.76	
100	730		1.76	826		1.99	850		2.05
		3.57			3.95			4.20	
156	930		1.49	1047		1.67	1085		1.78
		....			2.95			2.90	
218	....		....	1230		1.49	1265		1.53
		....			....			1.81	
306	....		....	....		....	1424		1.27

The results given under $\Lambda_{0(S)}/\Lambda_{0(KCl)}$ in table 139 show that the values of the equivalent conductance for complete ionization in the case of all the di-ionic substances investigated become more nearly equal as the temperature rises, the approach toward equality being rapid between 18° and 218°, but comparatively slow at the higher temperatures. This shows, of course, that the specific migration-velocities of the ions are themselves more nearly equal, the higher the temperature. Complete equality has not, however, been reached even at 306°, but the divergence exceeds 5 per cent only in the cases of hydrochloric acid, sodium hydroxide, and sodium acetate, which have ions which at 18° move with exceptionally large or small velocities.

The behavior of the tri-ionic salts, potassium sulphate and barium nitrate, is especially noteworthy. Their equivalent conductance increases steadily with rising temperature and attains values which are much greater than those for any di-ionic uni-univalent salt. Thus at 306° the value for potassium sulphate is about 1.5 times as great as that for potassium chloride. This behavior, which at first sight appears abnormal, is in reality in conformity with the principle that the velocities of ions subjected to the same electric force approach equality with rising temperature; for, assuming that the resistance of the medium becomes the same for all ions, the velocity of a bivalent ion, owing to its double electric charge, should become twice as great as that of a univalent ion under the same potential-gradient; and correspondingly, the equivalent conductance of a completely ionized unibivalent salt should become 1.5 times that of a completely ionized uni-univalent salt. What is remarkable is, therefore, not the greater values at high temperatures, but the approximate equality at room temperature of the equivalent conductances of bivalent and univalent ions, especially of the elementary ones which might be expected to have not far from the same size. This equality may be due, as has been suggested by Morgan and Kanolt,* to a relatively large hydration of the bivalent ions.

With respect to the form of the temperature-conductance curve, it will be seen from an examination of the values of $\Delta\Lambda_0/\Delta t$ that the rate of increase of conductance is in case of all the neutral di-ionic salts greater between 100° and 156° than it is between 18° and 100° or between 156° and 218°,† and therefore that the curve is first convex, later concave, and then again convex toward the temperature axis, with two intermediate points of inflexion.

In the case of the acids and bases, however, and therefore of the hydrogen-ion and the hydroxide-ion, the rate of increase of the equivalent

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*J. Am. Chem. Soc., **28**, 572 (1906).

†With respect to this last temperature-interval sodium acetate forms an exception.

conductance steadily decreases with rising temperature, so that the curve is always concave toward the temperature axis. With the tri-ionic salts, on the other hand, the rate of increase steadily increases, owing to the great increase in the equivalent conductance of the bivalent ion; the curve is therefore always convex toward the temperature axis.

It is of interest to note that the fluidity, or the reciprocal of the viscosity, of water shows nearly the same increase as the conductance of the di-ionic salts, at any rate up to 156°, which is about the limit to which previous determinations of the viscosity have extended. Thus, using for the viscosity (η) the data of Thorpe and Rodger and of de Haas* and taking the mean values of Λ_0 for the five uni-univalent salts included in this research, the product $\eta\Lambda_0$ has the values 1.19 at 18°, 1.04 at 100°, and 1.01 at 156°. When it is considered that the conductance values increase five-fold, this variation in the ratio will be seen to be of secondary significance.

With respect to the variation of the equivalent conductance (Λ) with the concentration (C), it has been found that between the concentrations 0.1 and 0.002 or 0.0005 normal the results at all temperatures with all the salts, both di-ionic and tri-ionic, and also with hydrochloric acid, nitric acid, and sodium hydroxide, are expressed by the function $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$ provided that to the exponent n a value (varying with the different substances) between 1.40 and 1.55 is assigned. This is clearly shown by the summary of the n values given in table 140. These were derived

TABLE 140.—*Values of exponent n in the function* $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$.

Substance.	18°.	100°.	156°.	218°.	281°.	306°.
KCl.	1.42	1.40	1.40	1.48	1.50	1.48
NaCl. . . .	1.42	1.48	1.50	1.50	1.47	1.46
$AgNO_3$ . .	1.53	1.52	1.50	1.50	1.52	1.52
$NaC_2H_3O_2$.	1.45	1.45	1.42	1.36	....	....
HCl.	1.45	1.38	1.40	1.47	....	....
HNO_3 . . .	1.43	1.45	1.45	....	....	....
NaOH . . .	1.50	1.50	1.50	....	....	....
$Ba(OH)_2$. .	1.55	1.45	1.45	....	....	....
K_2SO_4 . . .	1.42	1.42	1.42	1.42	1.42	1.42
$Ba(NO_3)_2$.	1.50	1.50	1.50	1.50	1.50	1.50
$MgSO_4$. . .	1.43	....	....	....	....	....

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*See Landolt-Börnstein-Meyerhoffer, Physikalisch-chemische Tabellen, pp. 76-77. From the data there given the viscosity in dynes per sq. cm. is found by interpolation to be 0.01052 at 18°, 0.00283 at 100°, and 0.001785 at 156°. The mean values of Λ_0 for the salts referred to are 113 at 18°, 369 at 100°, and 566 at 156°; the salts investigated were potassium, sodium, and ammonium chlorides, sodium acetate, and silver nitrate. Reference may also be made to the table given in Part II, page 53, in which a comparison is made between the change in fluidity and that in the equivalent conductance of potassium chloride for six temperature-intervals between 0° and 156°.

by a graphical method (see section 17, page 50) which involved no assumption in regard to the value of Λ_0, this being regarded as a third constant to be determined from the data themselves. In general, the value of n could be found within 0.02 or 0.03 units.

It is evident that, if the conductance-ratio Λ/Λ_0 can be taken as a measure of the ionization (γ), the latter changes with the concentration in the case of all these substances in accordance with an entirely similar exponential law, namely, in accordance with the function $\frac{(C\gamma)^n}{C(1-\gamma)} = \text{const.}$, in which n has values varying with different substances only between 1.40 and 1.55.

In a previous article* emphasis was laid on the remarkable fact that at ordinary temperature the form of the functional relation between ionization and concentration is the same for salts of different ionic types. These results show that this is also true at high temperatures, and, moreover, that even the very large variation of temperature here involved and the large consequent change in the character of the solvent affect only slightly, if at all, the value of the exponent in this purely empirical relation. Thus an additional confirmation is given to the important conclusion that the form of the concentration-function is independent of the number of ions into which the salt dissociates. This seems to show almost conclusively that chemical mass-action has no appreciable influence in determining the equilibrium between the ions and the un-ionized part of largely dissociated substances. How complete this contradiction with the mass-action law is, is seen when it is recalled that for di-ionic and tri-ionic salts this law requires that the concentration of the un-ionized substance be proportional to the square and cube, respectively, of the concentration of the ions, while the experimental data show that it is proportional to the $\frac{3}{2}$ power of that concentration, whatever may be the type of salt.

It has also been shown in the preceding articles (pages 49 and 139) that the functions $\Lambda_0 - \Lambda = KC^{\frac{1}{3}}$ and $\Lambda_0 - \Lambda = K(C\Lambda)^{\frac{1}{2}}$, which contain only two arbitrary constants (Λ_0 and K) satisfactorily express the results with potassium chloride, sodium chloride, hydrochloric acid, and sodium hydroxide at any rate up to 218° between the concentrations of 0.1 and 0.002 or 0.0005 normal. Since, however, the data at still smaller concentrations, as determined by Kohlrausch and others at 18°, do not conform to the requirements of these functions, they apparently do not give by extrapolation a correct value of Λ_0, and correspondingly the ratio Λ/Λ_0

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*Noyes, The Physical Properties of Aqueous Salt Solutions in Relation to the Ionic Theory, Congress of Arts and Science, St. Louis Exposition, **4**, 317 (1904); Technology Quarterly, **17**, 300 (1904); Science, **20**, 582 (1904); abstract in Z. phys. Chem., **52**, 635.

derived from them is not a true measure of the ionization. It has therefore not seemed worth while to make a study of the applicability of these functions to all the substances investigated.

The equivalent conductance and ionization of the slightly ionized substances, acetic acid and ammonium hydroxide, on the other hand, changes with the concentration at all temperatures even up to 306°, in accordance with the mass-action law. It is interesting to note that phosphoric acid, an acid of moderate ionization (60 per cent at 18° and 29 per cent at 156° at 0.01 normal concentration), has intermediate values of n $(1.8-1.9)$, which, however, approach more nearly the theoretical value (2.0) than the empirical one.

In order to show the relations between degree of ionization, the character of the substances, and the temperature, the percentage ionization of all the substances investigated at the different temperatures in 0.08 and 0.01 normal solution is shown in table 141. The substances are arranged in the order in which the ionization at 18° decreases. The values in the case of sulphuric acid show the percentage of the total hydrogen which exists in the form of hydrogen-ion, without reference to whether it arises through the primary dissociation into H^+ and HSO_4^- or the secondary one into H^+ and $SO_4^=$; the values are only approximate ones based on an estimate of the relative extent to which these two stages in the dissociation have taken place, as described on page 267. The values for magnesium sulphate are only rough approximations, owing to its being largely hydrolyzed.

The ionization at 0.08 normal for all of the salts and for hydrochloric and nitric acids is also shown graphically in figure 20.

Fig. 20.—Change of ionization with temperature.

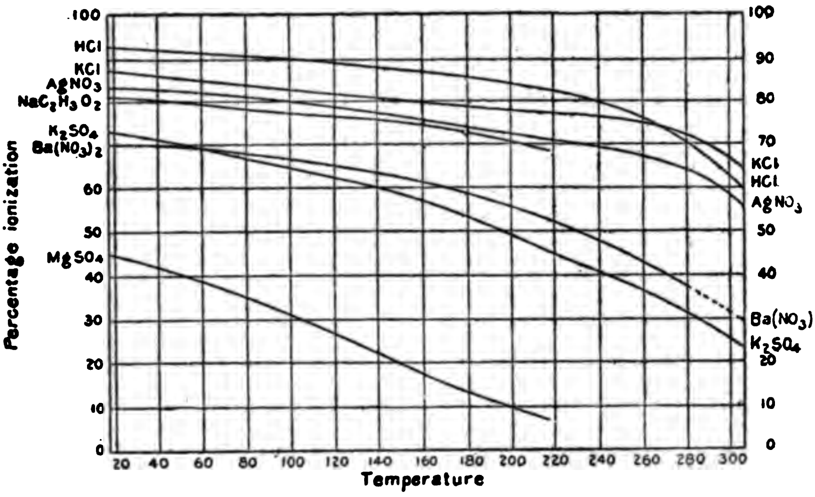

TABLE 141.—*Percentage ionization.*

Substance.	Concentration.	18°.		100°.		156°.		218°.		281°.		306°.	
		0.01	0.08	0.01	0.08	0.01	0.08	0.01	0.08	0.01	0.08	0.01	0.08
HCl	0.01	97.1	..	95.0	..	93.6	..	92.2	..		..	82	..
	0.08	..	93.2	..	89.7	..	87.2	..	82.5	..		..	60
HNO_3	0.01	96.8	..	95.2	..	93.4	..	..	..	..	..	..	..
	0.08	..	92.6	..	89.0	..	85.3	..	75	..	..	..	33
NaOH	0.01	96.2	..	95.7	..	94.3	..	92	..	..	..	..	..
KCl	0.01	94.2	..	91.1	..	89.7	..	89.8	..	87	..	81	..
	0.08	..	87.3	..	82.6	..	79.7	..	77.3	..	72	..	64
NaCl	0.01	93.6	..	92.7	..	92.1	..	90.2	..	84	..	80	..
	0.08	..	85.7	..	83.2	..	81.2	..	77.7	..	69	..	63
NH_4Cl	0.01	93.7	..	92.2	..	91.2	..	90.1	..	..	..	79	..
$AgNO_3$	0.01	93.3	..	91.8	..	88.8	..	86.3	..	82	..	77	..
	0.08	..	83.3	..	80.2	..	75.8	..	70.8	..	64	..	57
$NH_4C_2H_3O_2$	0.01	91.9	..	88.7	..	87.1	..	..	..	..	..	..	..
$NaC_2H_3O_2$	0.01	91.2	..	88.8	..	88.0	..	82.2	..	..	..	76	..
	0.08	..	81.1	..	77.6	..	75.6	..	68.5	..	..	..	..
$Ba(OH)_2$	0.01	93	..	85	..	85.	..	..	..	..	..	..	..
	0.08	..	83	..	70	..	65	..	..	..	..	..	..
K_2SO_4	0.01	87.2	..	80.3	..	75	..	63	..	47	..	37	..
	0.08	..	73.2	..	64.8	..	58	..	45	..	31	..	23
$Ba(NO_3)_2$	0.01	86.7	..	83.6	..	80	..	74	..	59	..	47	..
	0.08	..	70.1	..	66.9	..	62	..	53	..	38	..	..
H_2SO_4	0.01	83	..	56	..	49	..	46	..	..	..	..	..
	0.08	..	66	..	48	..	45	..	42	..	..	..	35
$MgSO_4$	0.01	66.7	..	52.4	..	35	..	13	..	..	..	..	..
	0.08	..	45.5	..	31.9	..	19	..	7	..	..	..	..
H_3PO_4	0.01	60	..	42	..	29.4	..	..	..	..	..	..	..
	0.08	..	31	..	19.5	..	12.5	..	..	..	..	..	..
$HC_2H_3O_2$	0.01	4.17	..	3.24	..	2.26	..	1.26	..	..	..	..	..
	0.08	..	1.50	..	1.17	..	0.82	..	0.46	..	..	..	0.14
NH_4OH	0.01	4.05	..	3.59	..	2.46	..	1.36	..	..	..	..	..
	0.08	..	1.45	..	..	..	..	..	0.47	..	..	..	0.11

As will be seen from table 141 the ionization steadily decreases with rising temperature in the case of every substance investigated. To this principle stated as an entirely general one the only exceptions seem to be water itself up to about 270° and many slightly ionized acids and bases up to about 40°, as illustrated by the ionization-constants for acetic acid and ammonium hydroxide tabulated below; but above this temperature, even such acids and bases also decrease steadily in ionization.*

The decrease in ionization will, moreover, be seen to be nearly the same for all the largely ionized salts of the same ionic type, so that such salts,

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*Compare also the results of Euler (Z. phys. Chem., **21**, 266, 1896) and of Schaller (Z. phys. Chem., **25**, 517, 1898).

which have roughly the same ionization at 18°, are also not far from equally ionized at much higher temperatures. The decrease in percentage ionization per ten degrees ($-10^2\Delta\gamma/\Delta t$) at the concentration 0.08 normal has for the neutral salts the following average values:

TABLE 142.—*Decrease of ionization with the temperature.*

Type of Salt.	Values of ($-10^2\Delta\gamma/\Delta t$) between				
	18° and 100°	100° and 156°	156° and 218°	218° and 281°	281° and 306°
Di-ionic	0.32	0.55	0.68	1.09	2.84
Tri-ionic	0.34	0.94	1.23	2.30	3.20

Thus the rate of decrease in ionization is small between 18° and 100° for either type of salt; but it becomes greater at the higher temperatures, especially in the case of the tri-ionic salts; and for the highest temperature-interval (281° - 306°) it is extremely rapid for both types of salt. The decrease in ionization of hydrochloric acid, nitric acid up to 156°, and sodium hydroxide is about the same as that of the di-ionic salts; thus the average value of ($-10^2\Delta\gamma/\Delta t$) at 0.08 normal for hydrochloric and nitric acids is 0.38 between 18° and 100°, 0.63 between 100° and 156°; and for hydrochloric acid 0.76 between 156° and 218°. Between 156° and 306° nitric acid decreases in ionization much more than the other substances of the same type.

The physical property of the solvent which is most closely related to its ionizing power is, as has been shown by Thomson and by Nernst, its dielectric constant. It is therefore of some interest to compare its variation with the temperature with that of the ionization of salts. Unfortunately, the dielectric constant of water has been determined only between 0° and 76°. Drude* has, however, derived for this interval a quadratic equation, from which a value at 100° may be calculated, probably without great error. The values of the dielectric constant obtained from this equation are 81.3 at 18° and 58.1 at 100°, and the ratio of these is 1.40.

The question now arises, what function of the ionization should be compared with this? It seems clear that, from a theoretical standpoint, it is simplest to consider the ratio $\frac{C_2(1-\gamma_2)}{C_1(1-\gamma_1)}$ of the concentrations of un-ionized salt which prevail in solutions that at the two temperatures (t_2 and t_1) have the same concentration of the ions (that is, solutions for which $C_2\gamma_2 = C_1\gamma_1$); for in such solutions the electric force between the ions, and therefore their tendency to unite to form un-ionized molecules, in so far as this has an electrical origin, must be inversely proportional to the dielec-

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*Wied. Ann. Phys., **59**, 50 (1896).

tric constant. The above ratio is evidently equivalent, since $C_2\gamma_2 = C_1\gamma_1$, to the ratio $\frac{(1-\gamma_2)/\gamma_1}{(1-\gamma_1)/\gamma_2}$, where, however, γ_1 and γ_2 refer to the slightly different concentrations C_1 and C_2 (C_2 being equal to $C_1\gamma_1/\gamma_2$).

Now for the four uni-univalent salts given in table 141 the mean values of the percentage ionization at 0.08 normal is 84.4 at 18° and 80.9 at 100°, or by interpolation, 80.6 at 100° at 0.08 × 1.042 normal (that is, at $C_1\gamma_1/\gamma_2$); whence the value of the ratio just referred to is found to be 1.30. The value of the corresponding ratio for the two tri-ionic salts at 0.08 normal is in the same way found to be 1.38.* While the former of these values differs considerably from the ratio (1.40) of the dielectric constants, yet all the values lie in the same neighborhood. Indeed, the agreement is as close as could be expected considering the character of the data involved.

Finally, even though it seems theoretically to correspond to a less comparable condition in the solution, yet, in view of the valence principle discussed just below, it is of interest to note the values of the simpler ratio, $\frac{C(1-\gamma_2)}{C(1-\gamma_1)}$, of the concentrations of the un-ionized substance at two temperatures at the same total concentration, instead of the same ion-concentration. At 0.08 the value of this ratio for 100°/18° is 1.22 for the four uni-univalent, and 1.21 for the two uni-bivalent salts, thus considerably less than the ratio of the dielectric-constants.

The degree of ionization of the different substances may be next considered in relation to the ionic type to which they belong and to their chemical nature. It has already been pointed out that even up to the highest temperatures neutral salts of the same ionic type have roughly the same percentage ionization, the differences not exceeding 8 per cent in any case investigated. The strong acids, hydrochloric acid and (up to 156°) nitric acid, and the strong bases, sodium and barium hydroxides, also conform in a general way to this principle, though their ionization seems to be several per cent greater than that of the corresponding salts; it is worthy of mention, however, that this greater value may be due to an increase in the equivalent conductance of the hydrogen-ion or hydroxide-ion with the concentration of the solute, as is indicated to be the case by the transference results with these acids presented in Part XI and again referred to below.

It is also remarkable that the rough proportionality which had previously been shown to exist at ordinary temperatures† between the un-ionized fraction of a salt at any concentration and the product of the valences of its ions has now been proved by the measurements of Noyes and Melcher to persist up to the highest temperatures, where the degree of ionization has become much less. This is shown by the following summary, which is a reproduction of table 29 on page 110. Under A are given the mean values of the percentage of un-ionized salt, $100(1-\gamma)$, for the neutral salts of each type at the concentration 0.04 molal and for the uni-univalent salts at 0.08 molal; and under B are given the ratios of these values to the product of the valences ($\nu_1\nu_2$) of the ions.

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*The mean values of the percentage ionization for these two salts at 0.08 normal are 71.7 at 18° and 65.8 at 100°, or by interpolation 64.8 at 100° at 0.08 × 1.09 normal.

†For a discussion of this principle, see the author's article on The Physical Properties of Aqueous Salt Solutions...., *loc. cit.*

ν_1 ν_2	Mols per liter.	18°		100°		156°		218°		281°		306°	
		A	B	A	B	A	B	A	B	A	B	A	B
1×1	0.04	12	12	15	15	17	17	20	20	25	25	31	31
1×1	0.08	15	15	18	18	21	21	25	25	31	31	39	39
1×2	0.04	28	14	34	17	40	20	51	25	65	32	74	37
2×2	0.04	55	14	68	17	81	20	93	23	..	..	..	..

It will be seen that the principle continues to hold, especially when the comparison is made at the same equivalent concentration, even when the ionization has become very small; thus it is only 26 per cent for the uni-bivalent salts at 306° and only 7 per cent for the bibivalent salt (magnesium sulphate) at 218°.

The ionization tendencies of phosphoric acid, acetic acid, and ammonium hydroxide, and the effect of temperature on them are best shown by the summary of their ionization-constants which is given in table 143.* The values for phosphoric acid were determined by Noyes and Eastman (see page 269), those for acetic acid by Noyes and Cooper (page 142) and by Sosman (page 228); and those for ammonium hydroxide were determined by Noyes and Kato (page 178), by Sosman (page 228), and by Kanolt (page 290). The concentration involved in the constant is expressed in equivalents per liter, and the constants themselves have been multiplied by 10^6.

It is evident from these results that the ionization-constant for ammonium hydroxide increases considerably in passing from 0° to 18°, then remains nearly constant up to 50°, and finally decreases with increasing rapidity as higher temperatures are reached, attaining at 306° a value which is only about one-two-hundredth of that at 18°; and that at all temperatures the values for acetic acid are not very different from those

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*In the case of phosphoric acid the values vary considerably with the concentration in correspondence with the fact that the exponent in the concentration-function was found to be 1.8 – 1.9 instead of 2 as required by the mass-action law. The values here given are those at the concentration 0.05 formula-weights (H_3PO_4) per liter.

TABLE 143.—*Ionization-constants of phosphoric acid, acetic acid, and ammonium hydroxide.*

Temperature.	Phosphoric acid.	Acetic acid.	Ammonium hydroxide.
0	....	....	13.9
0	10400	18.2	17.2
25	9400	....	18.0
50	7000	....	18.1
75	4800	....	16.4
100	3400	11.1	13.5
125	....	....	10.4
128	2230	....	....
156	1420	5.42	6.28
218	....	1.72	1.80
306	....	0.139	0.093

for ammonium hydroxide. Phosphoric acid is seen to have a much larger ionization, which, however, decreases steadily and very rapidly with rising temperature.

The interpretation of the results obtained with sulphuric acid is complicated by the fact that the ionization doubtless takes place in two stages; but a method has been described on pages 271-3 by which it is possible to determine the hydrogen-ion concentration within fairly narrow limits from the conductance alone, without knowledge of the extent to which the separate stages occur. The method is of general application to dibasic acids; and, if the ionization-constant for the first hydrogen be known, as is true with many of the organic acids, the method could be used for computing that of the second hydrogen from the conductance at high dilutions where the secondary ionization is appreciable. The ratio of the hydrogen-ion to the total hydrogen in the case of sulphuric acid is thus found to vary in 0.08 normal solution from about 66 per cent at 18° to 48 at 100° and 35 at 306°.

Similar calculations of the hydrogen-ion concentrations have been made in the case of potassium hydrogen sulphate. These show that in 0.1 molal solution at 156° the hydrogen-ion concentration is not more than 3 per cent; and this justifies the conclusion that the secondary ionization of sulphuric acid (into hydrogen-ion and sulphate-ion) in its own moderately concentrated solutions is also insignificant at this temperature and higher temperatures. Interpreted with the help of this conclusion the conductivity data for the acid show that the primary dissociation (into hydrogen-ion and hydrosulphate-ion) is about the same as that of hydrochloric acid at temperatures between 100° and 306°; and it is reasonable to suppose that the same is true at lower temperatures down to 18°.

With the help of this principle the ionization of the hydrosulphate-ion at 18°, 100°, and 156° in the solutions both of the acid and acid salt has been computed; the final results will be found in tables 118 and 119 on pages 274 and 276. This ionization is thus found to be large at 18°; but it decreases very rapidly with the temperature. Thus in a 0.1 molal potassium hydrogen sulphate solution equal quantities of sulphate-ion and hydrosulphate-ion are present at 18°; while at 100° there is only 15 per cent, and at 156° only 4 per cent, as much sulphate-ion as hydrosulphate-ion in the solution.

Only rough values of the ionization-constant of the hydrosulphate-ion into hydrogen-ion and sulphate-ion can be given, since they vary very much with the concentration; some idea of its magnitude is furnished by the following values which hold at about 0.01 molal (or 0.002 molal at 156°); 18500×10^{-6} at 18°, 1220×10^{-6} at 100°, and 115×10^{-6} at 156°, whereas the ionization-constant for acetic acid at 18° is 18×10^{-6}. From the change of the ionization-constant with the temperature, the heat absorbed (ΔU) by the reaction $HSO_4^- = H^+ + SO_4^=$ has been found to be given by the expression: $\Delta U = 14{,}170 - 65\ T$, where T represents the absolute temperature. From this it follows that the value at 18° is —4750 calories, and at 100°, —10,070 calories, while from Thomsen's heat-of-neutralization measurements and our ionization data at 18° the value —5020 calories is derived.

In addition to the measurements with unhydrolyzed salts just discussed there have been presented in the preceding Parts of this publication measurements of the conductance of certain salts of weak acids or bases both in water alone and in the presence of an excess of the acid or base. Various methods of calculating the hydrolysis from the change in conductance produced by the acid or base have been described (see pages 143, 186, and 230); and values of the hydrolysis of the salts in question have been obtained. From these, by combination with the ionization-constants of the acid and base, the ionization of water has been calculated. The salts so investigated are sodium acetate at 218° by A. A. Noyes and H. C. Cooper; ammonium acetate at 100°, 156°, 218°, and 306° by A. A. Noyes and Yogoro Kato and by R. B. Sosman; and the ammonium salt of diketotetrahydrothiazole, a very slightly ionized organic acid, at 0°, 18°, and 25° by C. W. Kanolt. The final conductance results will be found on pages 186, 188, 233 and 295.

Table 144 contains a summary of the computed values of the percentage hydrolysis of ammonium acetate in 0.01 normal solution, of the ionization-constant of water (defined by the equation $K_W = C_H . C_{OH}$), and of the concentration (C_H or C_{OH}) of the hydrogen-ion or hydroxide-ion in pure water in equivalents per liter. (The value for ammonium acetate at 18° is not based on direct measurements, but is calculated from the results of Kanolt with the ammonium salt of diketotetrahydrothiazole.)

TABLE 144.—*Hydrolysis of ammonium acetate and ionization of water.*

Temperature.	Hydrolysis of ammonium acetate.	Ionization-constant of water.	Hydrogen-ion concentration in pure water.
t	$100h$	$K_w \times 10^{14}$	$C_H \times 10^7$
0	....	0.089	0.30
18	(0.35)	0.46	0.68
25	....	0.82	0.91
100	4.8	48.	6.9
156	18.6	223.	14.9
218	52.7	461.	21.5
306	91.5	168.	13.0

It will be seen that the hydrogen-ion concentration in pure water increases with extraordinary rapidity between 0° and 100°; namely, by about 3 fold between 0° and 25° and 7½ fold between 25° and 100°. Between the latter temperature and 218° the ionization increases more slowly, afterwards passes through a maximum (which appears to lie between 250° and 275°), and finally decreases. When it is considered that the ionization of weak acids and bases, as shown by the data for ammonium hydroxide, acetic acid, and phosphoric acid, decreases rapidly with rising temperature, and that this acts in the same direction in increasing the hydrolysis of salts as does an increase in the ionization of water, it will be evident that the tendency of salts to hydrolyze is enormously greater at high temperatures, as is well illustrated by the values given for ammonium acetate.

The great increase in hydrolysis is also exemplified by the hydrolysis values for sodium acetate and ammonium chloride in 0.01 normal solution that can be calculated from the preceding data; these salts, which at 18° are 0.02 per cent hydrolyzed, are found to be 1.6 per cent at 218° and 3.4 to 4.1 per cent hydrolyzed at 306°.

The fact also deserves mention that the values of the concentration of the hydrogen-ion in water at 0°, 18°, and 25° as derived from these hydrolysis experiments are only 16 to 20 per cent lower than those obtained directly by Kohlrausch and Heydweiller* from the conductance of their purest water; thus proving that the ionization-constant of water is at any rate roughly the same when it is pure as when an ionized salt is present in it at a concentration of 0.02 to 0.05 normal.

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*Z. phys. Chem., **14**, 330 (1894).

From these ionization-constants (K_W) approximate values of the internal-energy-increase ΔU attending the reaction $H_2O = H^+ + OH^-$ (the so-called heat of ionization) can be computed by the familiar equation* derived from the Second Law of Energetics: $\frac{d \log K_W}{dT} = \frac{\Delta U}{RT^2}$

This is best done by integrating it under the assumption that ΔU is a linear function of the temperature as expressed by the equation $\Delta U = \Delta U_0 + \alpha RT$. The integral then has the form:

$$\log \frac{K_2}{K_1} - \alpha \log \frac{T_2}{T_1} = \frac{\Delta U_0}{R} \frac{T_2 - T_1}{T_1 T_2}$$

From the values of the ionization-constant K at 0°, 25°, and 100°, the values of the constants ΔU_0 and α have been found to be 28460 and -24.923, respectively. Therefore, the general equation for the energy-increase attending the ionization becomes:

$$\Delta U = 28460 - 49.5\,T,$$

and that for the ionization-constant becomes:

$$\log_{10}(10^{16}K) = 84.450 - \frac{6222}{T} - 24.923 \log_{10} T.$$

The values of the energy-increase in calories and of the ionization-constant of water as calculated by these expressions are given in table 145.

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*This equation ceases to be even approximately exact at high temperatures where the vapor-pressure of water becomes very large. The exact expression, which may be derived through the consideration of an appropriate cyclical process, is as follows:

$$\Delta U = RT^2 \frac{d \log K_W}{dT} + \Delta V . T^2 \left[\frac{d(p/T)}{dT} - \frac{d(P/T)}{dT} \right]$$

where ΔU is the energy-increase and ΔV is the volume-increase that attends the ionization of one mol of water under the pressure $p - P$, which is substantially identical with the vapor-pressure p, since the osmotic pressure P is in this case negligible in comparison. Approximate values of ΔV up to 140° have been computed by Tammann (Z. phys. Chem., **16**, 144. 1894) which show it to be equal to about -26 ccm. at 140°; and since it is shown to be increasing at a rate roughly proportional to the compressibility of water, it probably has a value in the neighborhood of -40 c. cm. at 218°. Assuming this to be the case, the last term in the above equation can, with the help of the existing vapor-pressure data, be shown to have a value of about -170 calories at 218°, while the value of ΔU as computed by the linear equation is 4155 at 218°. Thus at temperatures above 200° this last term begins to form a substantial part of the whole.

TABLE 145.—*Internal-energy-increase attending the ionization of water and its ionization-constant calculated by an empirical equation.*

Temperature.	Energy-increase ΔU	Ionization-constant $K \times 10^{14}$.
0	14950	0.088
18	14055	0.46
25	13710	0.81
50	12470	4.5
75	11230	16.9
100	9995	48.
128	8610	114.
156	7225	217.
218	(4155)	(512)

These values of the ionization-constant at 0°, 25°, and 100° necessarily agree with the directly determined ones given in table 144. It is of interest to note, however, that this is also true of the calculated value at 156°, which shows that up to this temperature the assumed equations hold true, and that therefore the values interpolated for the intermediate temperatures between 0° and 156° are doubtless substantially correct. Even at 218° the difference between the observed and calculated values (461 and 512), though doubtless real, is not very large; it lies in such a direction as to indicate that the energy-change ΔU is decreasing at a more rapid rate at temperatures above 156° than at the temperatures below it.

This is also shown by the fact that the ionization-constant at 306° is much less than at 218°, while according to the linear equation the value of ΔU should become zero, and therefore that of the ionization-constant K should become a maximum, very near the former temperature, namely, at 302°. The real maximum value of the constant seems to lie between 250° and 275°. Above this temperature ΔU assumes a negative value; and therefore the neutralization of completely ionized acids and bases would be attended by an absorption of heat.

It may also be mentioned that at the lower temperatures, the calculated values agree well with the heats of neutralization directly measured by Wörmann,† who found for hydrochloric and nitric acids when neutralized with potassium and sodium hydroxides as mean values 14,710 calories at 0° and 13,410 calories at 25°.

It seems worth while to call attention to a possible theoretical explanation of the fact that water, unlike all other substances thus far investigated, continues to increase in ionization up to so high a temperature as 250° to 275°. This phenomenon may well arise from the facts that water at low temperatures is a highly associated liquid containing only a small proportion of H_2O molecules, and that this proportion increases rapidly with rising temperature. Therefore, even though the fraction of H_2O molecules dissociated into H^+ and OH^- ions may decrease steadily, yet the actual concentration of these ions continues to increase until a large proportion of the complex water molecules have been depolymerized. This explanation was suggested by Dr. H. T. Kalmus of this laboratory.

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†Drude's Ann. Phys., **18**, 793 (1905).

Among the other results of these investigations, it deserves to be mentioned that, incidentally to the conductivity determinations, the specific volume of several solutions at 218°, 281°, and 306° was measured. That of the 0.002 normal solutions which can be regarded as identical with that of pure water, was found to be 1.187 at 218°, 1.337 at 281°, and 1.437 at 306°. By interpolating graphically from these results the value 1.305 is obtained for 270°. Ramsay and Young* found 1.188 at 218° and 1.300 at 270°, the highest temperature to which their measurements extended.

In addition to the conductivity researches at high temperatures, an investigation made by A. A. Noyes and Y. Kato of the ion-transference attending the electrolysis of solutions of hydrochloric and nitric acids at 20° has been described in this publication (in Part XI). The investigation was along the same lines as the one previously described by Noyes and Sammet.† Its main object was to determine what the value of the equivalent conductance of hydrogen-ion is and whether it varies to an important extent with the concentration.

The results will be found summarized in the table on page 327. It will be seen that the transference number of the anion in both nitric acid and hydrochloric acid decreases greatly as the concentration increases, and by a corresponding amount for the two acids up to 0.02 normal. This fact strongly indicates that hydrogen-ion, unlike the ions of neutral salts, increases in equivalent conductance or specific migration-velocity with increasing concentration, the magnitude of the increase being nearly five per cent between zero concentration and 0.02 normal. In deriving from conductivity data ionization values for largely ionized acids, it seems, therefore, most appropriate to divide the equivalent conductance at the concentration in question, not as usual by the equivalent conductance extrapolated for zero concentration, but by a value obtained by adding to the equivalent conductance of the anion that of the hydrogen-ion as derived from transference experiments at the same concentration. It is of interest to note that when this is done for hydrochloric and nitric acids at 20° their ionization is found to be nearly the same as that

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*Phil. Trans. (A), **183**, 109 (1882).

†J. Am. Chem. Soc., **24**, 958; **25**, 167 (1902-3); Z. phys. Chem., **43**, 63 (1903).

of neutral salts of the same ionic type instead of being several per cent larger as is the conductance-ratio Λ/Λ_0 taken in the usual way.

Reference may also be made to the measurements of Dr. Wilhelm Böttger, presented in Part X, of the solubility of some difficultly soluble salts. This constitutes only the beginning of a more extended investigation of the solubility of substances at high temperatures by means of conductance measurements. Results have thus far been obtained at 100° with silver chloride, bromide, and sulphocyanate, whose solubilities expressed in equivalents per million liters at 100° and 20° have been found to be as follows:

Temperature.	AgCl	AgSCN	AgBr
100	153	39	20
20	10.8	0.83	0.5
Ratio	14	46	40

In the preceding pages have been summarized the generalizations to be drawn from the results of these investigations, in regard to the behavior of the various types of chemical substances in aqueous solutions through a wide range of temperature. In conclusion, it seems, however, desirable to draw attention again to a theoretical principle of even more general import, which has been already presented in a previous article by the author as a conclusion apparently justified by a study of the then existing data; for this principle has now received a further confirmation through the demonstration of the fact that certain purely empirical laws relating to the ionization of salts in water still continue to be valid, even when the physical condition of that solvent is greatly altered by a large change in its temperature. This principle is that the ionization of salts, strong acids, and bases is a phenomenon primarily determined not by specific chemical affinities, but by electrical forces arising from the charges on the ions; that it is not affected (except in a secondary degree) by chemical mass-action, but is regulated by certain general, comparatively simple laws, fairly well established empirically, but of unknown theoretical significance; and that, therefore, it is a phenomenon quite distinct in almost all its aspects from the phenomenon of dissociation ordinarily exhibited by chemical substances, including that of the ionization of *weak* acids and bases.

The most important facts leading to this conclusion are the approximate identity of the ionization-values for salts of the same ionic type;

the existence of a simple approximate relation between the value of the un-ionized fraction and the product of the valences of the ions; the small effect of temperature on the ionization of salts and a parallelism between the magnitude of that effect and the effect upon the dielectric constant of water; the validity of an exponential relation between ionization and concentration, which differs from that required by the mass-action, and which is approximately the same at all temperatures and for different ionic types of salts; and the fact that the optical properties and other similar properties of dissolved salts (when referred to equal molal quantities) is independent of this concentration and therefore of their ionization, so long as the solution is even moderately dilute.

The molecular explanation of these facts and the more general conclusions drawn from them would seem to be that primarily the ions are united somewhat loosely in virtue of their electrical attraction to form molecules, the constituents of which still retain their electric charges and therefore to a great extent their characteristic power of producing optical effects and such other effects as are not dependent on their existence as separate aggregates. Secondly, the ions may unite in a more intimate way to form ordinary uncharged molecules, whose constituents have completely lost their identity and original characteristics. These two kinds of molecules may be designated electrical molecules and chemical molecules, respectively, in correspondence with the character of the forces which are assumed to give rise to them. Now in the case of salts and most of the inorganic acids and bases, the tendency to form chemical molecules is comparatively slight, so that the neutral electrical molecules greatly predominate. On the other hand, in the case of most of the organic acids, the tendency to form chemical molecules is very much greater, so that as a rule these predominate. The facts, moreover, indicate that chemical molecules are formed from the ions in accordance with the principle of mass-action,* but that electrical molecules are formed in accordance with an entirely distinct principle, whose theoretical basis is not understood.

It is to be expected that with neither class of substances will the predominating type of molecule be alone present; and that minor deviations from the mass-action law in the case of moderately ionized substances,

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*The best evidence of this is that furnished by the change of the conductivity of slightly ionized electrolytes with the concentration; but distribution experiments also indicate it. Thus it is probable that as a rule the chemical molecules alone distribute into the gaseous phase or into organic solvents and that therefore the concentration of the substance in such phases is a measure of the concentration of those molecules in the aqueous solution; and the few experiments thus far published indicate that the latter is at least approximately proportional to the product of the concentrations of the ions. (Compare the experiments on picric acid by Rothmund and Drucker, Z. phys. Chem., **46**, 826. 1903.)

and from the usual empirical law in the case of largely ionized substances, may well arise from the presence of a small proportion of molecules of the other type. In the former case, we may indeed with some confidence predict quantitatively that that proportion of electrical molecules will always be present which corresponds for the type of substance in question to the concentration of its ions in the solution.

A fuller experimental investigation of the properties of dissolved salts, especially of those of polyionic types, and of the phenomena of the solubility effect and the distribution into a gaseous or another liquid phase of ionizing substances, if combined with a thorough and persistent study of all the available data, gives promise of suggesting a fuller theoretical explanation of this remarkable behavior of largely ionized substances in aqueous solution. Even if such a theoretical interpretation should not be discovered, one may at least hope to determine with greater accuracy and certainty the laws of the equilibrium between the ions and un-ionized molecules, and between the two forms of the latter, in case their existence shall be more fully substantiated. It is my conviction that at any rate we have here to deal with a new kind of equilibrium phenomenon, and not simply with some deviation of a secondary nature, arising, for example from a somewhat abnormal osmotic pressure, or a change in the migration velocities of the ions, as has been assumed by most authors.

In conclusion I desire to express to the authorities of the Carnegie Institution my great indebtedness for the assistance rendered me in the prosecution of these researches; for without such aid the progress made would have been discouragingly slow.

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